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Evaluation of Expansion Coefficients from Optimal Fitting Parameters for the Analysis of Spectra of Diatomic Molecules and an Application to LiH

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To evaluate individual expansion coefficients composing fitting parameters of the Born–Oppenheimer corrections to Dunham's coefficients Y_{ij} that have been given analytically with the Δ_B and Δ_ω formalism, we examined the consistency of analytic expressions for those corrections with Watson's assertion of the experimental inseparability of nonadiabatic corrections $Q_{\mathrm{a,b}}(r)$ for a molecule *AB*. Derived analytic expressions in terms of optimal fitting parameters for the corrections are essential to evaluate individual expansion coefficients. These expressions also reveal redundancies between empirical correction parameters Δ_{ij}. A method of evaluating nonadiabatic vibrational corrections $Q_{\mathrm{a,b}}(r)$ and adiabatic corrections $S_{\mathrm{a,b}}(r)$ separately consistent with Watson's assertion of inseparability is presented and is applied to an analysis of spectral data of LiH. Functions $Q_{\mathrm{a,b}}$ and $S_{\mathrm{a,b}}$ for LiH are thus successfully evaluated; $S_{\mathrm{H,Li}}(r)$ values agree well with those predicted simply by wobble-stretch theory. Experimental values for optimal fitting parameters $r_{1\mathrm{q}}^{\mathrm{H}}$ and $r_{2\mathrm{q}}^{\mathrm{H}}$ are nearly equal to those of $r_{1\mathrm{q}}^{\mathrm{Li}}$ and $r_{2\mathrm{q}}^{\mathrm{Li}}$, respectively, in agreement with a theoretical relation $r_{i\mathrm{q}}^{\mathrm{a}} = r_{i\mathrm{q}}^{\mathrm{b}}$. **© 2001 Academic Press**

Key Words: Born–Oppenheimer correction; adiabatic; nonadiabatic correction; optimal parameter; expansion coefficient; redundancy; Δ_{ij}.

INTRODUCTION

Contemporary infrared and microwave spectrometers enable measurements of many spectral lines for diatomic molecules for many vibrational states and various isotopomers. To analyze such spectral lines considerations of adiabatic and nonadiabatic corrections to the Born–Oppenheimer approximation (*1–8*) are indispensable. A conventional method to take those corrections into account was to fit spectral lines to the (v, J) levels of a molecule *AB* expressed with a set of parameters that includes correction parameters $\Delta_{ij}^{\mathrm{a,b}}$ by Ross *et al.* (*9*), Bunker (*4*), and Watson (*2*). Watson discussed experimental inseparability of nonadiabatic vibrational effects $Q_{\mathrm{a,b}}(r)$ from nonadiabatic rotational $R_{\mathrm{a,b}}(r)$ and adiabatic $S_{\mathrm{a,b}}(r)$ effects. The correction parameters $\Delta_{ij}^{\mathrm{a,b}}$ have since been treated merely as empirical parameters for spectral fits (*10*).

Fernandez and Ogilvie provided, with hypervirial perturbation theory (*11*), analytic expressions for those corrections on the Dunham coefficients (*5*) expressing adiabatic and nonadiabatic effects in the Hamiltonian with a series expansion of $\xi[=(r-r_{\mathrm{e}})/r_{\mathrm{e}}]$ (*6*) or $z[=2(r-r_{\mathrm{e}})/(r+r_{\mathrm{e}})]$ (*5*). Following their analytic approach for the Born–Oppenheimer corrections, we modified the Δ_ω and Δ_B scheme of a potential model by Thompson *et al.* (*12*), with which we analyzed spectra of molecules (*13–15*), extending Dunham's treatment (*16, 17*) for the Schrödinger equation based on Watson's effective Hamiltonian (*2*), and obtained a compact expression for the contributions from the correction terms in the Hamiltonian to the Dunham Y_{ij} coefficients (*18–20*).

These results were applied to LiH (*18, 19*) and CaH molecules (*20*). Under the restriction of Watson's inseparability of $Q_{\mathrm{a,b}}(r)$ estimated values of fitting parameters for the corrections were considered to be effective, and we could not proceed (*18–20*) to relate values of fitting parameters to any physical quantities, e.g., molecular g_J values, electric dipole moments, and matrix elements of operators. Evaluation of individual expansion coefficients for $Q_{\mathrm{a,b}}(r)$, $R_{\mathrm{a,b}}(r)$, and $S_{\mathrm{a,b}}(r)$ from fitting parameters is necessary to relate values of fitting parameters to those physical quantities which can be expressed with expansion coefficients.

Analytic expressions of modified Dunham's Y_{ij} in terms of the Born–Oppenheimer correction parameters indicate that functions $Q_{\mathrm{a,b}}(r)$, $R_{\mathrm{a,b}}(r)$, and $S_{\mathrm{a,b}}(r)$ are experimentally separable if $R_{\mathrm{a,b}}(r)$ are estimated with experiments under the external fields or by theoretical calculation (*21, 22*). Ogilvie *et al.* (*21*) calculated functions of $R_{\mathrm{a,b}}(r)$ for LiH and, imposing those as constraints in a fit of spectral data of LiH, evaluated individual expansion coefficients for nonadiabatic vibrational functions $Q_{\mathrm{a,b}}(r)$ and adiabatic functions $S_{\mathrm{a,b}}(r)$ separately.

The purpose of this paper is to discuss evaluation of the individual expansion coefficients in detail from optimal fitting parameters that are clusters of expansion coefficients and can be estimated experimentally. Briefly, a consideration has resulted in an experimental method to evaluate $Q_{\mathrm{a,b}}(r)$ and $S_{\mathrm{a,b}}(r)$ separately from optimal fitting parameters that are consistent with

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the assertion of inseparability, with an aid of $R_{\mathrm{a,b}}(r)$ evaluated by Herman and Ogilvie's method (*22*) by the use of a rotational g factor $g_J(r)$ and an electric dipole moment function $M(r)$.

REVIEW OF AN ANALYTIC TREATMENT OF THE BORN–OPPENHEIMER BREAKDOWN FOR THE Δ_ω AND Δ_B FORMALISMS

In previous papers (*18–20*) we modified a model based on a scheme involving Δ_ω and Δ_B developed by Thompson *et al.* (*12*) including adiabatic and nonadiabatic correction terms for Born–Oppenheimer breakdown analytically in Dunham's coefficients Y_{ij}. We outline first the treatment of Ref. (*18*) to clarify definitions and notation.

With the original effective Hamiltonian of Ref. (*18*) after Watson (*2*) for diatomic molecules in electronic state $^1\Sigma$, the Schrödinger equation can be written in terms of a variable $\xi = (r - r_\mathrm{e})/r_\mathrm{e}$ as

$$\Bigg[-\frac{h^2}{8\pi^2\mu r_\mathrm{e}^2}\{1+(m_\mathrm{e}/M_\mathrm{a})Q_\mathrm{a}(\xi)+(m_\mathrm{e}/M_\mathrm{b})Q_\mathrm{b}(\xi)\}\frac{d^2}{d\xi^2} + \frac{h^2}{8\pi^2\mu r_\mathrm{e}^2(1+\xi)^2}\{1+(m_\mathrm{e}/M_\mathrm{a})R_\mathrm{a}(\xi)+(m_\mathrm{e}/M_\mathrm{b})R_\mathrm{b}(\xi)\} \times J(J+1) + V(\xi) + (m_\mathrm{e}/M_\mathrm{a})S_\mathrm{a}(\xi) + (m_\mathrm{e}/M_\mathrm{b})S_\mathrm{b}(\xi)\Bigg]\psi_{vJ}(\xi) = E_{vJ}(\xi)\psi_{vJ}(\xi), \qquad [1]$$

in which μ is the reduced mass of a molecule and M_a, M_b, and m_e are the masses of atoms A and B and the electron, respectively. Correction terms $-(h^2/8\pi^2\mu r_\mathrm{e}^2)\{(\delta Q')^2/[4(1+\delta Q)] - \delta Q''/2\}$, after Bunker and Moss (*23*), in which δQ denotes $(m_\mathrm{e}/M_\mathrm{a})Q_\mathrm{a}(\xi) + (m_\mathrm{e}/M_\mathrm{b})Q_\mathrm{b}(\xi)$, have been left out. They are smaller than $\left(m_\mathrm{e}/M_{\mathrm{a,b}}\right)S_{\mathrm{a,b}}(\xi)$ terms and generate corrections only for energy of orders higher than $\mathrm{O}(m_\mathrm{e}/M_{\mathrm{a,b}})$ (*8*).

Similarly to Dunham's original function for potential energy (*17*),

$$V(\xi) = (1/2)kr_\mathrm{e}^2\,\xi^2(1 + a_1\,\xi + a_2\,\xi^2 + \cdots), \qquad [2]$$

functions $Q_{\mathrm{a,b}}(\xi)$, $R_{\mathrm{a,b}}(\xi)$, and $S_{\mathrm{a,b}}(\xi)$ are expressed, after Fernandez and Ogilvie (*6*), as series expansions of ξ as

$$Q_{\mathrm{a,b}}(\xi) = \sum_{i=0} q_i^{\mathrm{a,b}}\xi^i, \qquad [3]$$

$$R_{\mathrm{a,b}}(\xi) = \sum_{i=0} r_i^{\mathrm{a,b}}\xi^i, \qquad [4]$$

and

$$S_{\mathrm{a,b}}(\xi) = \sum_{i=1} s_i^{\mathrm{a,b}}\xi^i, \qquad [5]$$

formally confining our attention to a region with $|\xi| < 1$. Three radial functions $Q(\xi)$, $R(\xi)$, and $S(\xi)$ serve as local representations (*6*); none is superfluous or subsidiary. Terms of $s_0^{\mathrm{a,b}}$ are removed from Eq. [5] because they yield no effect on Eq. [1] in the electronic ground state.

A treatment in Ref. (*18*) deriving Eq. [5] from the effective Hamiltonian [2] is incorrect. A wave function $\Psi_{vJ}(\xi)$ of Eq. [4] should be $A\psi_{vJ}(\xi)(1+\delta Q)^{-1/2}$ (*23*), in which A is a constant. A term $-(h^2/8\pi^2\mu r_\mathrm{e}^2)(\delta Q')^2/[4(1+\delta Q)]$ should be added to Eq. [5] in brackets [ ] on the left side. The corrections do not affect any other part of Ref. (*18*) or descriptions of Refs. (*19*) and (*20*).

Mass-independent functions $Q_{\mathrm{a,b}}(\xi)$, $R_{\mathrm{a,b}}(\xi)$, and $S_{\mathrm{a,b}}(\xi)$, are correction terms for nonadiabatic vibrational, nonadiabatic rotational, and adiabatic effects, respectively (*2*). The Hamiltonian [2] of Ref. (*18*) is written with a variable $\xi = (r - r_\mathrm{e})/r_\mathrm{e}$; in that sense, treatments of Ref. (*18*) are applicable to local representations near r_e in a region with $|\xi| < 1$. We assume that functions $Q_{\mathrm{a,b}}(\xi)$ are sufficiently well behaved functions (*6*). Our treatments do not include molecular ions; the reduced mass μ_C in Ref. (*18*) is replaced with μ.

According to Herman and Asgharian (*3*) we divide Eq. [1], ignoring terms of orders higher than $\mathrm{O}(m_\mathrm{e}/M_{\mathrm{a,b}})$, by

$$1 + (m_e/M_a)\sum_{i=1} q_i^a\xi^i + (m_e/M_b)\sum_{i=1} q_i^b\xi^i$$

to obtain

$$\Bigg[-\frac{h^2}{8\pi^2\mu r_\mathrm{e}^2}(1+\delta q_0)\frac{d^2}{d\xi^2} + \frac{h^2}{8\pi^2\mu r_\mathrm{e}^2(1+\xi)^2}(1+\delta r_0) \times\left(1+\sum_{i=1}\delta r_i'\,\xi^i\right)J(J+1) + (1/2)kr_\mathrm{e}^2\xi^2 \times\left\{1+\sum_{i=1}(a_i-\delta q_i)\,\xi^i\right\} + \sum_{i=1}\delta s_i'\xi^i\Bigg]\psi_{vJ}(\xi) = E_{vJ}\psi_{vJ}(\xi), \qquad [6]$$

in which

$$\delta q_i = (m_\mathrm{e}/M_\mathrm{a})\,q_i^\mathrm{a} + (m_\mathrm{e}/M_\mathrm{b})\,q_i^\mathrm{b}, \qquad [7]$$

$$\delta r_0 = (m_\mathrm{e}/M_\mathrm{a})\,r_0^\mathrm{a} + (m_\mathrm{e}/M_\mathrm{b})\,r_0^\mathrm{b}, \qquad [8]$$

$$\delta r_i' = (m_\mathrm{e}/M_\mathrm{a})\left(r_i^\mathrm{a} - q_i^\mathrm{a}\right) + (m_\mathrm{e}/M_\mathrm{b})\left(r_i^\mathrm{b} - q_i^\mathrm{b}\right), \qquad [9]$$

and

$$\delta s_i' = (m_\mathrm{e}/M_\mathrm{a})\left(s_i^\mathrm{a} + q_i^\mathrm{a}E_{vJ}\right) + (m_\mathrm{e}/M_\mathrm{b})\left(s_i^\mathrm{b} + q_i^\mathrm{b}E_{vJ}\right). \qquad [10]$$

The following notation δx_i is used hereafter for a pair of arbitrary quantities x_i^a and x_i^b:

$$\delta x_i = (m_\mathrm{e}/M_\mathrm{a})\,x_i^\mathrm{a} + (m_\mathrm{e}/M_\mathrm{b})\,x_i^\mathrm{b}. \qquad [11]$$

A quantity E_{vJ} that appears in $\delta s_i'$ on the left side of Eq. [6] can be expressed as a known power-series expansion in $(v + 1/2)$ and $J(J + 1)$ (*3*); E_{vJ} in $\delta s_i'$ is treated as a known constant (*18*). Similar expressions are utilized by Molski (*24*) and Coxon and Hajigeorgiou (*25*) after Herman and Ogilvie (*22*), denoting E_{vJ} on the left side as E_{vJ}^{BO}. Using Eq. [6] has the advantage that it yields clusters of expansion coefficients Δ_B and Δ_ω for B_e and ω_e, respectively (*3*). E_{vJ} terms on the left side (E_{vJ}^{BO}) are minute corrections but accompany $q_\mathrm{i}^{\mathrm{a,b}}$, which prevents other clusters of expansion coefficients from being optimal fitting parameters.

Equation [6] is rewritten in terms of a variable $\eta = (r - r_\mathrm{e}')/r_\mathrm{e}'$,

$$\Bigg[-\frac{h^2(1+g_1)}{8\pi^2\mu r_\mathrm{e}^2}\frac{d^2}{d\eta^2} + \frac{h^2(1+g_2)}{8\pi^2\mu r_\mathrm{e}^2(1+\eta)^2} \times\left(1+\sum_{i=1}\delta r_i'\eta^i\right)J(J+1) + (1/2)kr_\mathrm{e}^2(1+g_3)\eta^2 \times\left(1+\sum_{i=1}k_i\eta^i\right)\Bigg]\psi_{vJ}(\eta) = E_{vJ}\psi_{vJ}(\eta), \qquad [12]$$

in which

$$g_1 = \delta q_0 + \left(2/kr_\mathrm{e}^2\right)\delta s_1', \qquad [13]$$

$$g_2 = \delta r_0 + \left(2/kr_\mathrm{e}^2\right)\delta s_1', \qquad [14]$$

and

$$g_3 = -\left(1/kr_\mathrm{e}^2\right)\{(2+3a_1)\delta s_1' - 2\delta s_2'\}, \qquad [15]$$

in which the vibrational energy, B_e in the rotational energy, and Dunham's $hca_0(=kr_\mathrm{e}^2/2)$ within the Born–Oppenheimer approximation are corrected with small quantities, g_1, g_2, and g_3, respectively. The internuclear distance r_e' represents the minimum of the function for the effective potential energy composed of Dunham's $V(\xi)$ plus an adiabatic correction and small terms including E_{vJ}. Further details of notation in Eqs. [1] and [12] are given in Ref. (*18*).

Details of Dunham's WKB treatment applied to Eq. [12] that are not presented explicity in Ref. (*18*) are given in the Appendix.

The application of Dunham's treatment yields vibrational–rotational energy $F_{vJ}(=E_{vJ}/hc)$ as

$$F_{vJ} = \sum_{ij} Y_{ij}^{*vJ}(v+1/2)^i[J(J+1)]^j. \qquad [16]$$

Modified Dunham coefficients $Y_{ij}^{*vJ(0)}$ given in Refs. (*18*) and (*19*) for $ij = 01$, 02, 03, 04, 10, 11, 12, 20, and 21 are analytic expressions that include correction parameters $\Delta_B^{\mathrm{a,b}}$, $\Delta_\omega^{\mathrm{r\,a,b}}$, $\Delta_{ai}^{\mathrm{a,b}}\,(i = 1, 2, \ldots)$, $r_i'^{\,\mathrm{a,b}}\,(i = 0, 1, 2, \ldots)$, and $q_i^{\mathrm{a,b}}(i = 1, 2, \ldots)$, in which $q_i^{\mathrm{a,b}}\,(i = 1, 2, \ldots)$ are those accompanied with E_{vJ} terms on the left side of Eq. [6].

Dunham obtained Y_{ij} in a power series with a ratio $(B_\mathrm{e}/\omega_\mathrm{e})^2$,

$$Y_{ij} = Y_{ij}^{(0)} + Y_{ij}^{(2)} + Y_{ij}^{(4)} + \cdots, \qquad [17]$$

in which $Y_{ij}^{(0)}$ means the lowest order term in Y_{ij} in the series with the ratio $(B_\mathrm{e}/\omega_\mathrm{e})^2$, i.e., $Y_{ij}^{(0)}$ is the leading contribution of Y_{ij} that corresponds to $U_{ij}\mu^{-(i+2j)/2}$ (*26*). Since $Y_{ij}^{(0)}, Y_{ij}^{(2)}, \ldots$ include corrections $\Delta_B^{\mathrm{a,b}}, \Delta_\omega^{\mathrm{r\,a,b}}, \Delta_{ai}^{\mathrm{a,b}}\,(i = 1, 2, \ldots)$, $r_i'^{\,\mathrm{a,b}}\,(i = 0, 1, 2, \ldots)$, and $q_i^{\mathrm{a,b}}\,(i = 1, 2, \ldots)$ we use the notations $Y_{ij}^{*\,vJ(0)}$, $Y_{ij}^{*\,vJ(2)}, \ldots$. The symbol $*$ means that $Y_{ij}^{(n)}$ includes correction parameters. The superscript vJ signifies that $Y_{it}^{(n)}$ includes small correction terms of F_{vJ} which originate from the left side of Eq. [6].

To discuss the consistency of Eq. [6] with Watson's effective Hamiltonian with $\tilde{R}_{\mathrm{a,b}}$ and $\tilde{S}_{\mathrm{a,b}}$, we should extract small F_{vJ} terms in Y_{ij}^{*vJ} by expanding F_{vJ} as a known power series in $Y_{ij}(v+1/2)^i[J(J+1)]^j$ of the Born–Oppenheimer expansion. The rearranged series expansion has term coefficients $Y_{ij}^{*}(=Y_{ij}^{*(0)} + Y_{ij}^{*(2)} + \cdots)$. Eight relevant $Y_{ij}^{*(0)}\,(ij = 01$, 02, 03, 04, 10, 11, 12, and 20) have been given in Refs. (*18*) and (*19*). Now, a set of 8 modified Dunham coefficients $Y_{ij}^{*(0)}$ includes 10 δ correction parameters, $\delta\Delta_B$, $\delta\Delta_\omega^\mathrm{r}$, $\delta\Delta_{a1}^\mathrm{s}$, $\delta\Delta_{a2}^\mathrm{s}$, δr_1, δr_2, δr_3, $\delta r_0'$, δq_1, and δq_2, in which $\delta\Delta_{a1}^\mathrm{s}$, $\delta\Delta_{a2}^\mathrm{s}$ are defined by the equations

$$\begin{aligned} a_1^\mathrm{s} &= a_1\left(1+\delta\Delta_{a1}^\mathrm{s}\right) \\ &= a_1^{\mathrm{d}'} = a_1\left[1-\left(2B_\mathrm{e}/\omega_\mathrm{e}^2\right)\right. \\ &\quad\left.\times\{(1-3a_1+4a_2/a_1)\delta s_1 + 2\delta s_2 - 2\,\delta s_3/a_1\}\right], \end{aligned} \qquad [18]$$

and

$$\begin{aligned} a_2^\mathrm{s} &= a_2\left(1+\delta\Delta_{a2}^\mathrm{s}\right) = a_2^{\mathrm{d}'} + a_1\delta q_1 \\ &= a_2\left[1-\left(2B_\mathrm{e}/\omega_\mathrm{e}^2\right)\{(2-3a_1+5a_3/a_2)\delta s_1\right. \\ &\quad\left. + 2\delta s_2 - 2\,\delta s_4/a_2\}\right]. \end{aligned} \qquad [19]$$

Quantities $a_1^{\mathrm{d}'}$ and $a_2^{\mathrm{d}'}$ have been defined in Ref. (*19*).

Our treatment of Eq. [6] is an extension of Dunham's WKB approach. However, a perturbation treatment (*27*) of Eq. [6] results in exactly the same expression for $Y_{ij}^{*vJ(0)}$ as was referred to in Ref. (*19*). When we apply Kilpatrick's perturbation treatment (*27*) of a vibrator to our case, we obtain exactly the same equation as Eq. [A.64]. In order to proceed the solution to that of a rotating–vibrating molecule, he has introduced a variable to remove a linear term in ξ of the centrifugal energy. The treatment of the change of variable is also identical to our treatment given in Eq. [A.61].

The agreement of results in Refs. (*18*) and (*19*) with those produced with a hypervirial perturbation treatment by Fernandez and Ogilvie (*6*) is described in Ref. (*19*).

CORRESPONDENCE OF $Y_{ij}^{*(0)}$ TO Δ_{ij}

Modified Dunham coefficients $Y_{ij}^{*(0)}$ can be written as

$$\begin{aligned} Y_{ij}^{*(0)} &= Y_{ij}^{(0)}\{1+\delta(\text{correction terms})_{ij}\} \\ &= Y_{ij}^{(0)}\Big[1+\big(m_\mathrm{e}/M_\mathrm{a}\big)\Big\{\big(\Delta_{ij}^{\mathrm{a}}\big)^{\mathrm{ad}}+\big(\Delta_{ij}^{\mathrm{a}}\big)^{\mathrm{nonad}}\Big\} \\ &\quad +(m_\mathrm{e}/M_\mathrm{b})\Big\{\big(\Delta_{ij}^{\mathrm{b}}\big)^{\mathrm{ad}}+\big(\Delta_{ij}^{\mathrm{b}}\big)^{\mathrm{nonad}}\Big\}\Big] \\ &= Y_{ij}^{(0)}\Big\{1+(m_\mathrm{e}/M_\mathrm{a})\Delta_{ij}^{\mathrm{adnad,\,a}}+(m_\mathrm{e}/M_\mathrm{b})\Delta_{ij}^{\mathrm{adnad,\,b}}\Big\}, \end{aligned} \quad [20]$$

under the assumption that we can neglect the Born–Oppenheimer correction terms of orders higher than $O(m_\mathrm{e}/M_{\mathrm{a,b}})$. A term $\delta(\text{correction terms})_{ij}$ means the portion of the δ correction terms in $Y_{ij}^{*(0)}$. According to Watson (*1*) and Tiemann *et al.* (*10*), Δ_{01} includes the Dunham correction in addition to the adiabatic, $(\Delta_{01}^{\mathrm{a,b}})^{\mathrm{ad}}$, and the nonadiabatic, $(\Delta_{01}^{\mathrm{a,b}})^{\mathrm{nonad}}$, parts. We can naturally extend those quantities of $i, j = 0, 1$ to other i, j. As the magnitude of $Y_{ij}^{(2)}$ is smaller than $Y_{ij}^{(0)}$ by a factor $(B_\mathrm{e}/\omega_\mathrm{e})^2$, the Dunham correction to Δ_{ij} is $(\mu/m_\mathrm{e}Y_{ij}^{(0)})Y_{ij}^{(2)}$; i.e.,

$$\begin{aligned} &(m_\mathrm{e}/M_\mathrm{a})\Delta_{ij}^{\mathrm{a}}+(m_\mathrm{e}/M_\mathrm{b})\Delta_{ij}^{\mathrm{b}} \\ &\quad = (m_\mathrm{e}/M_\mathrm{a})\Big\{\Delta_{ij}^{\mathrm{adnad,a}}+\big(\mu/m_\mathrm{e}Y_{ij}^{(0)}\big)Y_{ij}^{(2)}\Big\} \\ &\qquad +(m_\mathrm{e}/M_\mathrm{b})\Big\{\Delta_{ij}^{\mathrm{adnad,b}}+\big(\mu/m_\mathrm{e}Y_{ij}^{(0)}\big)Y_{ij}^{(2)}\Big\} \\ &\quad = \delta(\text{correction terms})_{ij}+\big(1/m_\mathrm{e}Y_{ij}^{(0)}\big)Y_{ij}^{(2)}. \end{aligned} \quad [21]$$

Equation [21] gives the correspondence of $Y_{ij}^{*(0)}$ to Δ_{ij}. Expressions for $\delta(\text{correction terms})_{ij}$ can be obtained with Eq. [20]; e.g.,

$$\delta(\text{correction terms})_{01} = \delta\Delta_B = \delta r_0 + \big(4B_\mathrm{e}/\omega_\mathrm{e}^2\big)\delta s_1. \quad [22]$$

EVALUATION OF EXPANSION COEFFICIENTS FROM EXPERIMENTAL FREQUENCY DATA

Consistency of our result of an analytic approach with Watson's assertion of inseparability should be discussed with explicit expressions for $Y_{ij}^{*(0)}$.

We confine our attention to a level of a set of 8 $Y_{ij}^{*(0)}$, i.e., $Y_{01}^{*(0)}$, $Y_{02}^{*(0)}$, $Y_{03}^{*(0)}$, $Y_{04}^{*(0)}$, $Y_{10}^{*(0)}$, $Y_{11}^{*(0)}$, $Y_{12}^{*(0)}$, and $Y_{20}^{*(0)}$. In these 8 quantities $Y_{ij}^{*(0)}$, 10 correction parameters appear, $\delta\Delta_B$, $\delta\Delta_\omega^{\mathrm{r}}$, $\delta\Delta_{a1}^{\mathrm{s}}$, $\delta\Delta_{a2}^{\mathrm{s}}$, δr_1, δr_2, δr_3, $\delta r_0'$, δq_1, and δq_2, in which

$$\delta\Delta_\omega^{\mathrm{r}} = \delta r_0/2 - \big(B_\mathrm{e}/\omega_\mathrm{e}^2\big)(3a_1\,\delta s_1 - 2\,\delta s_2) \quad [23]$$

and expressions for $\delta\Delta_{\mathrm{a1}}^{\mathrm{s}}$ and $\delta\Delta_{\mathrm{a2}}^{\mathrm{s}}$ are given in Eqs. [18] and [19], respectively. These 8 $Y_{ij}^{*(0)}$ coefficients suffice for most practical purposes. If further $Y_{ij}^{*(0)}$ at higher levels need to be taken into account, other δ parameters must be correspondingly included. As the number of experimentally determinable $Y_{ij}^{*(0)}$ is 8 for this level of the parameter set of each isotopomer, at most 8 δ parameters can be evaluated from experiment. Only 7 parameters, rather than 8, can actually be evaluated independently because of redundancy between $\delta\Delta^{\mathrm{adnad}}$, as is described below.

As a first step, a criterion is to select 8 independent clusters, made from 10 δ, that can be solved analytically to be expressed in terms of 8 experimental values, i.e., values of 8, $Y_{ij}^{*(0)}$. The clusters of δ parameters can then be experimentally evaluated. Calculations are made with a symbolic processor, REDUCE. In all discussion we assume that correction terms of orders higher than $O(m_\mathrm{e}/M_{\mathrm{a,b}})$ are negligible.

Clusters of δ parameters are selected most readily with reference to Watson's $\tilde{R}_{\mathrm{a,b}}$ and $\tilde{S}_{\mathrm{a,b}}$ (*2*). As $\tilde{R}_{\mathrm{a,b}}$ and $\tilde{S}_{\mathrm{a,b}}$ are expressed in terms of a variable denoting internuclear distance, r, we rewrite them with a reduced variable ξ, as

$$\tilde{R}_{\mathrm{a,b}}(\xi) = R_{\mathrm{a,b}}(\xi) - \frac{1}{1+\xi}\int_{\xi 0}^{\xi} Q_{\mathrm{a,b}}(\xi)\,d\xi = \sum_{i=0} \tilde{r}_i^{\mathrm{a,b}}\xi^i, \quad [24]$$

$$\tilde{S}_{\mathrm{a,b}}(\xi) = S_{\mathrm{a,b}}(\xi) + \frac{1}{2}\frac{dV(\xi)}{d\xi}\int_{\xi 0}^{\xi} Q_{\mathrm{a,b}}(\xi)\,d\xi = \sum_{i=0} \tilde{s}_i^{\mathrm{a,b}}\xi^i, \quad [25]$$

in which

$$\begin{aligned} &\big\{\tilde{r}_0^{\mathrm{a,b}}, \tilde{r}_1^{\mathrm{a,b}}, \tilde{r}_2^{\mathrm{a,b}}, \tilde{r}_3^{\mathrm{a,b}}\big\} \\ &\quad = \Big\{r_0^{\mathrm{a,b}} - P\big(\xi_0^{\mathrm{a,b}}\big), r_1^{\mathrm{a,b}} + P\big(\xi_0^{\mathrm{a,b}}\big) - q_0^{\mathrm{a,b}}, r_2^{\mathrm{a,b}} - P\big(\xi_0^{\mathrm{a,b}}\big) + q_0^{\mathrm{a,b}} \\ &\qquad - q_1^{\mathrm{a,b}}/2, r_3^{\mathrm{a,b}} + P\big(\xi_0^{\mathrm{a,b}}\big) - q_0^{\mathrm{a,b}} + q_1^{\mathrm{a,b}}/2 - q_2^{\mathrm{a,b}}/3\Big\}, \end{aligned} \quad [26]$$

and

$$\begin{aligned} &\big\{\tilde{s}_0^{\mathrm{a,b}}, \tilde{s}_1^{\mathrm{a,b}}, \tilde{s}_2^{\mathrm{a,b}}, \tilde{s}_3^{\mathrm{a,b}}, \tilde{s}_4^{\mathrm{a,b}}\big\} \\ &\quad = \Big\{s_0^{\mathrm{a,b}}, s_1^{\mathrm{a,b}} + \big(\omega_\mathrm{e}^2/4B_\mathrm{e}\big)P\big(\xi_0^{\mathrm{a,b}}\big), \\ &\qquad s_2^{\mathrm{a,b}} + \big(\omega_\mathrm{e}^2/4B_\mathrm{e}\big)\big(3a_1P\big(\xi_0^{\mathrm{a,b}}\big)/2 + q_0^{\mathrm{a,b}}\big), \\ &\qquad s_3^{\mathrm{a,b}} + \big(\omega_\mathrm{e}^2/2B_\mathrm{e}\big)\big(a_2P\big(\xi_0^{\mathrm{a,b}}\big) + 3a_1q_0^{\mathrm{a,b}}/4 + q_1^{\mathrm{a,b}}/4\big), \\ &\qquad s_4^{\mathrm{a,b}} + \big(\omega_\mathrm{e}^2/2B_\mathrm{e}\big)\big(5a_3P\big(\xi_0^{\mathrm{a,b}}\big)/4 + a_2q_0^{\mathrm{a,b}} \\ &\qquad + 3a_1q_1^{\mathrm{a,b}}/8 + q_2^{\mathrm{a,b}}/6\big)\Big\}, \end{aligned} \quad [27]$$

in which ξ_0 corresponds to Watson's arbitrary value for a lower limit of integration and $P(\xi_0^{\mathrm{a,b}})$ is a definite integral of $Q_{\mathrm{a,b}}(\xi)$ from $\xi_0^{\mathrm{a,b}}$ to 0. Physical significance of ξ_0 is not clear (*6*) but we use this as a formal parameter. These equations indicate eight clusters of expansion coefficients, $\delta\tilde{r}_0$, $\delta\tilde{r}_1$, $\delta\tilde{r}_2$, $\delta\tilde{r}_3$, $\delta\tilde{s}_1$, $\delta\tilde{s}_2$, $\delta\tilde{s}_3$, and $\delta\tilde{s}_4$.

Watson (*2*) eliminated $\delta\tilde{r}_0$ setting $P(\xi_0^{\mathrm{a,b}}) = r_0^{\mathrm{a,b}}$. It is clear from Eqs. [26] and [27] that one cannot eliminate $r_0^{\mathrm{a,b}}$ from

$Y_{ij}^{*(0)}$ by such a treatment, as has been remarked also by Coxon and Hajigeorgiou (*25*).

Watson's $\tilde{R}_{\mathrm{a,b}}$ and $\tilde{S}_{\mathrm{a,b}}$ imply that a replacement of $\{\delta q_0, \delta q_1, \delta q_2, \delta r_0, \delta r_1, \delta r_2, \delta r_3, \delta s_1, \delta s_2, \delta s_3, \delta s_4\}$ in expressions $Y_{ij}^{*(0)}$ with $\{0, 0, 0, 0, \delta\tilde{r}_1, \delta\tilde{r}_2, \delta\tilde{r}_3, \delta\tilde{s}_1, \delta\tilde{s}_2, \delta\tilde{s}_3, \delta\tilde{s}_4\}$ setting $P(\xi_0^{\mathrm{a,b}}) = r_0^{\mathrm{a,b}}$ reproduces exactly the same expressions for $Y_{ij}^{*(0)}$. We confirm this for our analytical expressions of $Y_{ij}^{*(0)}$ as follows.

Retaining $P(\xi_0^{\mathrm{a,b}})$ as an arbitrary quantity in the 8 clusters of coefficients, a replacement of

$$\begin{aligned}&\left\{\delta q_0, \delta q_1, \delta q_2, \delta r_0, \delta r_1, \delta r_2, \delta r_3, \delta s_1, \delta s_2, \delta s_3, \delta s_4\right\}\\ &\quad\to \left\{0, 0, 0, \delta\tilde{r}_0, \delta\tilde{r}_1, \delta\tilde{r}_2, \delta\tilde{r}_3, \delta\tilde{s}_1, \delta\tilde{s}_2, \delta\tilde{s}_3, \delta\tilde{s}_4\right\}\end{aligned}$$

applied to a set of 10 δ parameters $\{\delta\Delta_B, \delta\Delta_\omega^{\mathrm{r}}, \delta\Delta_{\mathrm{a1}}^{\mathrm{s}}, \delta\Delta_{\mathrm{a2}}^{\mathrm{s}}, \delta r_0', \delta r_1, \delta r_2, \delta r_3, \delta q_1, \delta q_2\}$ yields 8 clusters of parameters,

$$\begin{aligned}&\left\{\delta\Delta_B, \delta\Delta_\omega^{\mathrm{r}} - \delta P(\xi_0)/2 + \delta q_0/2,\right.\\ &\quad \delta\Delta_{\mathrm{a1}}^{\mathrm{s}} - \delta P(\xi_0)/2 + \delta q_0/2 + \delta q_1/(2a_1),\\ &\quad \delta\Delta_{\mathrm{a2}}^{\mathrm{s}} - \delta P(\xi_0) + \delta q_0 + 3a_1\delta q_1/(4a_2) + \delta q_2/(3a_2),\\ &\quad \delta r_0 - \delta P(\xi_0), \delta r_1 + \delta P(\xi_0) - \delta q_0,\\ &\quad \delta r_2 - \delta P(\xi_0) + \delta q_0 - \delta q_1/2,\\ &\quad \left.\delta r_3 + \delta P(\xi_0) - \delta q_0 + \delta q_1/2 - \delta q_2/3, 0, 0\right\}\\ &\equiv \{8 \text{ clusters}, 0, 0\}. \qquad [28]\end{aligned}$$

Then a replacement

$$\begin{aligned}&\left\{\delta\Delta_B, \delta\Delta_\omega^{\mathrm{r}}, \delta\Delta_{\mathrm{a1}}^{\mathrm{s}}, \delta\Delta_{\mathrm{a2}}^{\mathrm{s}}, \delta r_0', \delta r_1, \delta r_2, \delta r_3, \delta q_1, \delta q_2\right\}\\ &\quad\to \{8 \text{ clusters}, 0, 0\}\end{aligned}$$

applied to $Y_{ij}^{*(0)}$, given in Refs. (*18*) and (*19*), reproduces identical expressions for $Y_{ij}^{*(0)}$. The arbitrary quantity $\delta P(\xi_0)$ vanishes. Therefore, it is confirmed that a replacement of $\{\delta q_0, \delta q_1, \ldots, \delta r_0, \delta r_1, \ldots, \delta s_1, \delta s_2, \ldots\}$ in expressions of $Y_{ij}^{*(0)}$ with $\{0, 0, \ldots, \delta\tilde{r}_0, \delta\tilde{r}_1, \ldots, \delta\tilde{s}_1, \delta\tilde{s}_2, \ldots\}$ yields exactly the same energy expressions; Watson's effective Hamiltonian with $\tilde{R}_{\mathrm{a,b}}$ and $\tilde{S}_{\mathrm{a,b}}$ yields the same analytic expressions as $Y_{ij}^{*(0)}$.

Proceeding to the next step, the system determinant to solve those eight equations for eight unknowns, i.e., the eight clusters of parameters without $\delta P(\xi_0)$, is calculated symbolically to be zero with REDUCE; these eight equations have one or more redundancies. Since $\delta P(\xi_0)$ vanishes it is left out. When a component, $\delta\tilde{r}_0$, among {eight clusters, 0, 0} is absorbed into other clusters, the expressions of the eight $Y_{ij}^{*(0)}$ can eventually be rewritten by the use of a set of seven combined δ parameters, i.e., correction parameters of $\delta\Delta_B$ and six parameters given by

$$\delta\Delta_\omega = \delta\Delta_\omega^{\mathrm{r}} - \delta r_0'/2, \qquad [29]$$

$$\delta\Delta_{a1\mathrm{q}} = \delta\Delta_{a1}^{\mathrm{s}} - \delta r_0'/2 + \delta q_1/2a_1, \qquad [30]$$

$$\delta\Delta_{a2\mathrm{q}} = \delta\Delta_{a2}^{\mathrm{s}} - \delta r_0' + 3a_1\delta q_1/4a_2 + \delta q_2/3a_2, \qquad [31]$$

$$\delta r_{1q} = \delta r_1 + \delta r_0', \qquad [32]$$

$$\delta r_{2q} = \delta r_2 - \delta r_0' - \delta q_1/2, \qquad [33]$$

and

$$\delta r_{3\mathrm{q}} = \delta r_3 + \delta r_0' + \delta q_1/2 - \delta q_2/3. \qquad [34]$$

We call these seven clusters of the expansion coefficients optimal fitting parameters hereafter. The optimal fitting parameters can be solved analytically to be expressed with seven appropriate experimental values of $Y_{ij}^{*(0)}$. Quantities $\delta r_{i\mathrm{q}}$ ($i = 1, 2$, and 3) are identical with $\delta\tilde{r}_i$ ($i = 1, 2$, and 3) under the condition that $P(\xi_0^{\mathrm{a,b}}) = r_0^{\mathrm{a,b}}$:

$$\delta r_{i\mathrm{q}} = \delta\tilde{r}_i, \quad \left[i = 1, 2, 3 \text{ and } P\left(\xi_0^{\mathrm{a,b}}\right) = r_0^{\mathrm{a,b}}\right]. \qquad [35]$$

Optimal parameters $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{\mathrm{a1q}}$, and $\delta\Delta_{\mathrm{a2q}}$ are corrections of the type of δp_i in $p_i(1 + \delta p_i)$ in which p_i represents one of B_{e}, ω_{e}, a_1, or a_2, respectively, and $\delta r_{1\mathrm{q}}$, $\delta r_{2\mathrm{q}}$, and $\delta r_{3\mathrm{q}}$ are those of successive ξ^i ($i = 1, 2$, and 3) terms of a series expansion of the rotational parameter $B(\xi)$; i.e., optimal fitting parameters comprise corrections for $B_{\mathrm{e}}, \omega_{\mathrm{e}}, a_1, a_2, a_3, \ldots,$ and those for successive terms of a power series expansion [ξ^i ($i = 1, 2, 3, \ldots$) terms] for $B(\xi)$.

Modified Dunham coefficients $Y_{ij}^{*(0)}$ written by those parameters are given as

$$Y_{01}^{*(0)} = B_{\mathrm{e}}^{\mathrm{d}} = B_{\mathrm{e}}(1 + \delta\Delta_B), \qquad [36]$$

$$\begin{aligned}Y_{02}^{*(0)} &= -\left(4B_{\mathrm{e}}^{\mathrm{d3}}/\omega_{\mathrm{e}}^2\right)(1 - 2\,\delta\Delta_\omega - \delta r_{1\mathrm{q}})\\ &= -[4\{B_{\mathrm{e}}(1 + \delta\Delta_B)\}^3/\{\omega_{\mathrm{e}}(1{+}\delta\Delta_\omega)\}^2](1 - \delta r_{1\mathrm{q}}), \qquad [37]\end{aligned}$$

$$\begin{aligned}Y_{03}^{*(0)} &= \left(16B_{\mathrm{e}}^{\mathrm{d5}}/\omega_{\mathrm{e}}^4\right)\{3 + a_1 - 4(3 + a_1)\delta\Delta_\omega + a_1\delta\Delta_{a1\mathrm{q}}\\ &\quad - (5 + 3a_1/2)\delta r_{1\mathrm{q}} + \delta r_{2\mathrm{q}}\}\\ &= [16\{B_{\mathrm{e}}(1 + \delta\Delta_B)\}^5/\{\omega_{\mathrm{e}}(1 + \delta\Delta_\omega)\}^4]\\ &\quad \times\{3 + a_1(1 + \delta\Delta_{a1\mathrm{q}}) - (5 + 3a_1/2)\delta r_{1\mathrm{q}} + \delta r_{2\mathrm{q}}\}, \qquad [38]\end{aligned}$$

$$\begin{aligned}Y_{04}^{*(0)} &= \left(16B_{\mathrm{e}}^{\mathrm{d}\,7}/\omega_{\mathrm{e}}^6\right)\big\{-52 - 36a_1 + 4a_2 - 9a_1^2\\ &\quad + 6\left(52 + 36a_1 - 4a_2 + 9a_1^2\right)\delta\Delta_\omega\\ &\quad - 36a_1\delta\Delta_{a1\mathrm{q}} + 4a_2\delta\Delta_{a2\mathrm{q}} - 18a_1^2\delta\Delta_{a1\mathrm{q}}\\ &\quad + \left(120 + 78a_1 - 8a_2 + 18a_1^2\right)\delta r_{1\mathrm{q}}\\ &\quad - (32 + 12a_1)\delta r_{2\mathrm{q}} + 4\delta r_{3\mathrm{q}}\big\}\\ &= [16\{B_{\mathrm{e}}(1 + \delta\Delta_B)\}^7/\{\omega_{\mathrm{e}}(1 + \delta\Delta_\omega)\}^6]\\ &\quad \times\big[-52 - 36a_1(1 + \delta\Delta_{a1\mathrm{q}})\\ &\quad + 4a_2(1 + \delta\Delta_{a2\mathrm{q}}) - 9\{a_1(1 + \delta\Delta_{a1\mathrm{q}})\}^2\\ &\quad + \left(120 + 78a_1 - 8a_2 + 18a_1^2\right)\delta r_{1\mathrm{q}}\\ &\quad - (32 + 12a_1)\delta r_{2\mathrm{q}} + 4\delta r_{3\mathrm{q}}\big], \qquad [39]\end{aligned}$$

$$Y_{10}^{*(0)} = \omega_e(1 + \delta\Delta_\omega), \tag{40}$$

$$\begin{aligned}Y_{11}^{*(0)} &= (B_e^{d\,2}/\omega_e)\{6(1 + a_1) - 6(1 + a_1)\delta\Delta_\omega \\ &\quad + 6a_1\,\delta\Delta_{a1q} - (4 + 3a_1)\delta r_{1q} + 2\,\delta r_{2q}\} \\ &= [\{B_e(1 + \delta\Delta_B)\}^2/\{\omega_e(1 + \delta\Delta_\omega)\}] \\ &\quad \times \{6 + 6a_1(1 + \delta\Delta_{a1q}) - (4 + 3a_1)\delta r_{1q} + 2\delta r_{2q}\},\end{aligned} \tag{41}$$

$$\begin{aligned}Y_{12}^{*(0)} &= \left(B_e^{d4}/\omega_e^3\right)\left\{-114 - 108a_1 + 48a_2 - 54a_1^2\right. \\ &\quad + 3\left(114 + 108a_1 - 48a_2 + 54a_1^2\right)\delta\Delta_\omega \\ &\quad - 108\left(a_1 + a_1^2\right)\delta\Delta_{a1q} + 48a_2\delta\Delta_{a2q} \\ &\quad + \left(144 + 126a_1 - 48a_2 + 54a_1^2\right)\delta r_{1q} \\ &\quad \left. - (60 + 36a_1)\delta r_{2q} + 24\,\delta r_{3q}\right\} \\ &= [\{B_e(1 + \delta\Delta_B)\}^4/\{\omega_e(1 + \delta\Delta_\omega)\}^3] \\ &\quad \times [-114 - 108a_1(1 + \delta\Delta_{a1q}) \\ &\quad + 48a_2(1 + \delta\Delta_{a2q}) - 54\{a_1(1 + \delta\Delta_{a1q})\}^2 \\ &\quad + \left(144 + 126a_1 - 48a_2 + 54a_1^2\right)\delta r_{1q} \\ &\quad - (60 + 36a_1)\delta r_{2q} + 24\delta r_{3q}\big],\end{aligned} \tag{42}$$

and

$$\begin{aligned}Y_{20}^{*(0)} &= -\left(B_e^d/8\right)\left\{3\left(5a_1^2 - 4a_2\right) + 30a_1^2\delta\Delta_{a1q} - 12a_2\delta\Delta_{a2q}\right\} \\ &= -\{B_e(1 + \delta\Delta_B)/8\}[15\{a_1(1 + \delta\Delta_{a1q})\}^2 \\ &\quad - 12a_2(1 + \delta\Delta_{a2q})].\end{aligned} \tag{43}$$

Watson's treatment in which $\tilde{R}_{a,b}(\xi = 0)$ is made to vanish by setting $P(\xi_0^{a,b}) = r_0^{a,b}$ signifies that only seven clusters are independent. Equations [36]–[43] can also be obtained by simply replacing $\{\delta q_0, \delta q_1, \delta q_2, \delta r_0, \delta r_1, \delta r_2, \delta r_3, \delta s_1, \delta s_2, \delta s_3, \delta s_4\}$ in expressions of $Y_{ij}^{*(0)}$ in Refs. (*18*) and (*19*) with clusters of $\{0, 0, 0, 0, \delta\tilde{r}_1, \delta\tilde{r}_2, \delta\tilde{r}_3, \delta\tilde{s}_1, \delta\tilde{s}_2, \delta\tilde{s}_3, \delta\tilde{s}_4\}$, in which conditions $P(\xi_0^{a,b}) = r_0^{a,b}$ are applied.

Therefore, one can use a set of expansion coefficients of $\tilde{R}_{a,b}$ and $\tilde{S}_{a,b}$, i.e., $\delta\tilde{r}_1$, $\delta\tilde{r}_2$, $\delta\tilde{r}_3$, $\delta\tilde{s}_1$, $\delta\tilde{s}_2$, $\delta\tilde{s}_3$, and $\delta\tilde{s}_4$, as optimal fitting parameters, instead of $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$, $\delta\Delta_{a2q}$, δr_{1q}, δr_{2q}, and δr_{3q}, replacing $\{\delta q_0$, δq_1, δq_2, δr_0, δr_1, δr_2, δr_3, δs_1, δs_2, δs_3, $\delta s_4\}$ in $Y_{ij}^{*(0)}$ in Refs. (*18*) and (*19*) with $\{0, 0, 0, 0, \delta\tilde{r}_1, \delta\tilde{r}_2, \delta\tilde{r}_3, \delta\tilde{s}_1, \delta\tilde{s}_2, \delta\tilde{s}_3, \delta\tilde{s}_4\}$, which are related to expansion coefficients for $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$ by Eqs. [26] and [27]. However, if analytical expressions for $Y_{ij}^{*(0)}$ are not utilized when one uses $\delta\tilde{r}_i$ and $\delta\tilde{s}_i$ as fitting parameters, one must take redundancies between $Y_{ij}^{*(0)}$ explicitly into account so as not to estimate incorrectly some parameters on introduction of correction terms of order $O(m_e^2/M_{a,b}^2)$ unexpectedly. Redundancies exist only within the approximation that correction terms of the orders higher than $O(m_e/M_{a,b})$ are ignored. A set of fitting parameters $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$, $\delta\Delta_{a2q}$, $\delta r_{1q}(= \delta\tilde{r}_1)$, $\delta r_{2q}(= \delta\tilde{r}_2)$, and $\delta r_{3q}(= \delta\tilde{r}_3)$ has simpler physical significance than that of $\delta\tilde{r}_1$, $\delta\tilde{r}_2$, $\delta\tilde{r}_3$, $\delta\tilde{s}_1$, $\delta\tilde{s}_2$, $\delta\tilde{s}_3$, and $\delta\tilde{s}_4$.

REDUNDANCIES BETWEEN $Y_{ij}^{*(0)}$ OR $\delta\Delta_{ij}^{\mathrm{adnad}}$

As the eight $Y_{ij}^{*(0)}$ coefficients of Eqs. [36]–[43] are expressed with only seven independent parameters for Born–Oppenheimer corrections, one redundancy exists among these eight $Y_{ij}^{*(0)}$ or $\delta\Delta_{ij}^{\mathrm{adnad}}$. More redundancies exist with sets of $Y_{ij}^{*(0)}$ or equivalently $\delta\Delta_{ij}^{\mathrm{adnad}}$ at higher levels. A redundancy that exists in five $Y_{ij}^{*(0)}$ at the level of eight $Y_{ij}^{*(0)}$, i.e., $Y_{03}^{*(0)}$, $Y_{04}^{*(0)}$, $Y_{11}^{*(0)}$, $Y_{12}^{*(0)}$, and $Y_{20}^{*(0)}$, is

$$\begin{aligned}24(6 + a_1)C_{03} + 6C_{04} - 6(1 - a_1)C_{11} - C_{12} + 2C_{20} \\ = 6\left(13 + 18a_1 + 5a_1^2\right)C_{10} - 120C_{02},\end{aligned} \tag{44}$$

in which

$$C_{03} = \left(\omega_e^4/16B_e^5\right)Y_{03}^{*(0)} - (3 + a_1), \tag{45}$$

$$C_{04} = \left(\omega_e^6/16B_e^7\right)Y_{04}^{*(0)} + \left(52 + 36a_1 - 4a_2 + 9a_1^2\right), \tag{46}$$

$$C_{11} = \left(\omega_e/B_e^2\right)Y_{11}^{*(0)} - 6(1 + a_1), \tag{47}$$

$$C_{12} = \left(\omega_e^3/B_e^4\right)Y_{12}^{*(0)} + \left(114 + 108a_1 - 48a_2 + 54a_1^2\right), \tag{48}$$

and

$$C_{20} = (8/B_e)Y_{20}^{*(0)} - \left(12a_2 - 15a_1^2\right). \tag{49}$$

As the lowest level of a set of three $Y_{ij}^{*(0)}$, i.e., $Y_{01}^{*(0)}$, $Y_{02}^{*(0)}$, and $Y_{10}^{*(0)}$, includes just three parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, and δr_{1q}, those $Y_{ij}^{*(0)}$ coefficients have no redundancy. Therefore, C_{02} and C_{10} on the right side of Eq. [44] should be fixed to

$$C_{02} = \left(\omega_e^2/4B_e^3\right)Y_{02}^{*(0)} + 1, \tag{50}$$

$$C_{10} = \delta\Delta_\omega. \tag{51}$$

With explicit expressions of Eq. [20] for $\delta\Delta_{ij}^{\mathrm{adnad}}$, Eq. [44] provides redundancy between $\delta\Delta_{03}^{\mathrm{adnad}}$, $\delta\Delta_{04}^{\mathrm{adnad}}$, $\delta\Delta_{11}^{\mathrm{adnad}}$, $\delta\Delta_{12}^{\mathrm{adnad}}$, and $\delta\Delta_{20}^{\mathrm{adnad}}$. Three parameters, $\delta\Delta_B$, $\delta\Delta_\omega$ and δr_{1q}, can be directly estimated from the lowest level of a set of three $Y_{ij}^{*(0)}$.

Redundancy between Δ_{ij} should be considered when one analyzes spectra with empirical Δ_{ij} parameters. If analytical expressions for $Y_{ij}^{*(0)}$ are utilized, fits with optimal correction parameters eliminate any problem of redundancy between Δ_{ij}.

APPLICATION

In order to test the present expressions to evaluate individual expansion coefficients, we have analyzed data of lithium hydride utilized in a previous work (*19*) plus that of additional rotational transitions (*28*): 151 rotational and 354 vibrational–rotational FTS measurements (*29*), 27 vibrational–rotational diode laser measurements (*29*), 22 (*30*) plus 19 (*28*) rotational measurements with tunable far-infrared spectrometers, and 10 millimeter-wave measurements (*31*, *32*). We have selected spectral data of 19 transitions from Ref. (*28*) which are not reported in Ref. (*30*). In total 583 spectral lines for four isotopomers of lithium hydride are analyzed using Eqs. [36]–[43]. Other Y_{ij} and higher order contributions $Y_{ij}^{(2)}$ are taken from Bouanich (*33*), Woolley (*34*), Ogilvie and Bouanich (*35*), Ogilvie and Tipping (*36*), and Uehara (*19*); explicitly, 21 $Y_{ij}^{(0)}$, i.e., ij = 05, 06, 07, 08, 13, 14, 15, 16, 21, 22, 23, 24, 30, 31, 32, 33, 40, and 41, and 9 $Y_{ij}^{(2)}$, i.e., 01, 02, 03, 10, 11, 12, 20, 21, and 30, are added in the analysis. Other terms of greater order with $Y_{ij}^{(n\geq 4)}$ are excluded.

Transitions of four isotopomers are fitted simultaneously to a model retaining 20 adjustable parameters, $U_\omega(=\mu^{1/2}\omega_e)$, $U_B(=\mu B_e)$, $a_1, a_2, a_3, a_4, a_5, a_6, a_7$, $\Delta_\omega^{\mathrm{H}}$, $\Delta_\omega^{\mathrm{Li}}$, Δ_B^{H}, Δ_B^{Li}, $r_{1\mathrm{q}}^{H}$, $r_{1\mathrm{q}}^{\mathrm{Li}}$, $r_{2\mathrm{q}}^{\mathrm{H}}$, $r_{2\mathrm{q}}^{\mathrm{Li}}$, $r_{3\mathrm{q}}^{\mathrm{H}}$, $\Delta_{a1\mathrm{q}}^{\mathrm{H}}$, and $\Delta_{a2\mathrm{q}}^{\mathrm{H}}$, in which 11 later ones are the optimal fitting parameters for corrections. Other parameters are set to zero. These parameters are connected with the vibrational–rotational energy levels through $Y_{ij}^{*(0)}$, $Y_{ij}^{(0)}$, and $Y_{ij}^{(2)}$, described above. Weights of measured frequencies are assumed to be proportional to $(1/\delta_{\mathrm{obs}})^2$ except 19 transitions of Ref. (*28*) for which we used their obs-calc values for values of δ_{obs}. Atomic masses are taken from Audi and Wapstra (*37*). With 20 parameters the normalized standard deviation of the fit is 1.12, substantially equal to that obtained previously (*19*). The molecular parameters determined in the present fit are shown in Table 1.

TABLE 1
Dunham Potential Constants and Optimal Fitting Parameters for Corrections for Lithium Hydride

Born-Oppenheimer Parameters		Optimal Fitting Parameters for Corrections	
U_B /cm^{-1}u^1	6.627 099 7(17) [a]	Δ_B^{H}	-1.557 85(21)
U_ω/cm^{-1}u$^{1/2}$	1319.946 8(11)	Δ_B^{Li}	-0.109 9(29)
a_1	-1.897 225(13)	$\Delta_\omega^{\mathrm{H}}$	-0.675 1(16)
a_2	2.443 88(12)	$\Delta_\omega^{\mathrm{Li}}$	-0.106 9(66)
a_3	-2.630 19(45)	$\Delta_{a1\mathrm{q}}^{\mathrm{H}}$	0.487(50)
a_4	2.483 4(24)	$\Delta_{a2\mathrm{q}}^{\mathrm{H}}$	0.89(19)
a_5	-2.115(15)	$r_{1\mathrm{q}}^{\mathrm{H}}=\tilde{r}_1^{\mathrm{H}}$	0.739(13)
a_6	1.631(41)	$r_{1\mathrm{q}}^{\mathrm{Li}}=\tilde{r}_1^{\mathrm{Li}}$	0.807(70)
a_7	-0.890(81)	$r_{2\mathrm{q}}^{\mathrm{H}}=\tilde{r}_2^{\mathrm{H}}$	-2.03(29)
		$r_{2\mathrm{q}}^{\mathrm{Li}}=\tilde{r}_2^{\mathrm{Li}}$	-1.82(38)
		$r_{3\mathrm{q}}^{\mathrm{H}}=\tilde{r}_3^{\mathrm{H}}$	4.35(64)
reduced standard deviation = 1.12			

[a] The uncertainty (one standard error) in the last digits is given in parentheses.

In Table 2, expressions of the optimal fitting parameters in terms of expansion coefficients are reproduced. Those clusters of the coefficients can be resolved through functions for rotational g factor $g_J(\xi)$ and an electric dipole moment function $M(\xi)$. Herman and Ogilvie (*22*) provided relations between nonadiabatic expansion coefficients $r_i^{\mathrm{a,b}}$ and $g_J(\xi)$ and $M(\xi)$ to estimate $r_i^{\mathrm{a,b}}$ utilized in the spectral analysis,

$$g_J(\xi)=\sum_{i=1}\left\{(m_{\mathrm{p}}/M_{\mathrm{a}})r_i^{\mathrm{a}}+(m_{\mathrm{p}}/M_{\mathrm{b}})r_i^{\mathrm{b}}\right\}\xi^i=(m_{\mathrm{p}}/m_{\mathrm{e}})\sum_{i=1}\delta r_i\xi^i \tag{52}$$

and

$$2M(\xi)/\{er_{\mathrm{e}}(1+\xi)\}=\sum_{i=1}\left(r_i^{\mathrm{b}}-r_i^{\mathrm{a}}\right)\xi^i. \tag{53}$$

Equation [53] is defined for a molecule AB of relative polarity $^{-}AB^{+}$.

If functions of $g_J(\xi)$ and $M(\xi)$ for LiH are available by another means (*21*), we can estimate $r_i^{\mathrm{H,Li}}$ $(i = 0, 1, 2, \text{and } 3)$ with which values of the fitting parameters $\Delta_\omega^{\mathrm{H,Li}}$, $\Delta_B^{\mathrm{H,Li}}$, $r_{1\mathrm{q}}^{\mathrm{H,Li}}$, $r_{2\mathrm{q}}^{\mathrm{H,Li}}$, $r_{3\mathrm{q}}^{\mathrm{H,Li}}$, $\Delta_{a1\mathrm{q}}^{\mathrm{H,Li}}$, and $\Delta_{a2\mathrm{q}}^{\mathrm{H,Li}}$ can be resolved to yield expansion coefficients $q_i^{a,b}$ and $s_i^{a,b}$. Coefficients $s_1^{\mathrm{H,Li}}$, $q_0^{\mathrm{H,Li}}$, $q_1^{\mathrm{H,Li}}$, $q_2^{\mathrm{H,Li}}$, $s_2^{\mathrm{H,Li}}$, $s_3^{\mathrm{H,Li}}$, and $s_4^{\mathrm{H,Li}}$ are obtained successively from $\Delta_B^{\mathrm{H,Li}}$, $r_{1\mathrm{q}}^{\mathrm{H,Li}}$, $r_{2\mathrm{q}}^{\mathrm{H,Li}}$, $r_{3\mathrm{q}}^{\mathrm{H,Li}}$, $\Delta_\omega^{\mathrm{H,Li}}$, $\Delta_{a1\mathrm{q}}^{\mathrm{H,Li}}$, and $\Delta_{a2\mathrm{q}}^{\mathrm{H,Li}}$, respectively. In Table 2 each expansion coefficient is listed on the right side of the corresponding optimal fitting parameter.

The rotational g factor $g_J(\xi)$ and the electric dipole-moment function $M(\xi)$ can be determined from experiments under external fields. Therefore, the above procedure means that nonadiabatic vibrational, $Q_{\mathrm{a,b}}(\xi)$, nonadiabatic rotational, $R_{\mathrm{a,b}}(\xi)$, and adiabatic, $S_{\mathrm{a,b}}(\xi)$, effects are completely separable by experiments if one accepts Herman and Ogilvie's relation [52] and [53]. As $Y_{01}^{*(0)}$ includes only one determinable parameter $\delta\Delta_B$ given in Eq. [20] and does not include $q_i^{\mathrm{a,b}}$, accepted physical significance of the rotational constant B_{e} (*1, 38*) is justified.

Only in this way can one resolve clusters of expansion coefficients in the present absence of reliable estimates of $q_i^{\mathrm{a,b}}$ or $s_i^{\mathrm{a,b}}$ by another appropriate means. In a fit of spectral data of LiH, Ogilvie *et al.* (*21*) constrained a function $R_{\mathrm{H,Li}}(\xi)$ to values calculated from the rotational g factor and electric dipole moment and evaluated individual values of expansion coefficients. The present approach of an evaluation of expansion coefficients is substantially the same as that of Ogilvie *et al.* (*21*), although they chose s_3^{H} (in the present notation, q_3^{H}), instead of s_2^{H}, as a fitting parameter. The essence of the present approach is in an optimal selection of fitting parameters that are clusters of expansion coefficients.

Therefore, one cannot estimate the rotational g factor and the electric dipole moment from pure rotational and vibrational–rotational spectra unless relevant values of $q_i^{\mathrm{a,b}}$ or $s_i^{\mathrm{a,b}}$ are estimated by other sources or neglected (*39, 40*). To evaluate

TABLE 2
Expansion Coefficients for Lithium Hydride

Expressions for Optimal Fitting Parameters	Expansion Coefficients		Wobble-Stretch Theory[a]
$\Delta_B^{\mathrm{H}} = r_0^{\mathrm{H}} + (4B_e/\omega_e^2)s_1^{\mathrm{H}}$	$s_1^{\mathrm{H}}/10^5\ \mathrm{cm}^{-1}$	-0.527 93(14)[b]	-0.527
$\Delta_B^{\mathrm{Li}} = r_0^{\mathrm{Li}} + (4B_e/\omega_e^2)s_1^{\mathrm{Li}}$	$s_1^{\mathrm{Li}}/10^5\ \mathrm{cm}^{-1}$	-0.581 1(19)	-0.527
$\Delta_\omega^{\mathrm{H}} = -(B_e/\omega_e^2)(3a_1s_1^{\mathrm{H}} - 2s_2^{\mathrm{H}}) + q_0^{\mathrm{H}}/2$	$s_2^{\mathrm{H}}/10^5\ \mathrm{cm}^{-1}$	0.769 2(87)	0.790
$\Delta_\omega^{\mathrm{Li}} = -(B_e/\omega_e^2)(3a_1s_1^{\mathrm{Li}} - 2s_2^{\mathrm{Li}}) + q_0^{\mathrm{Li}}/2$	$s_2^{\mathrm{Li}}/10^5\ \mathrm{cm}^{-1}$	1.142(47)	0.790
$\Delta_{a1q}^{\mathrm{H}} = -(2B_e/\omega_e^2)\{(1 - 3a_1 + 4a_2/a_1)s_1^{\mathrm{H}} + 2s_2^{\mathrm{H}} - 2s_3^{\mathrm{H}}/a_1\}$ $-(r_0^{\mathrm{H}} - q_0^{\mathrm{H}})/2 + q_1^{\mathrm{H}}/2a_1$	$s_3^{\mathrm{H}}/10^5\ \mathrm{cm}^{-1}$	-1.04(20)	-1.053
$\Delta_{a2q}^{\mathrm{H}} = -(2B_e/\omega_e^2)\{(2 - 3a_1 + 5a_3/a_2)s_1^{\mathrm{H}} + 2s_2^{\mathrm{H}} - 2s_4^{\mathrm{H}}/a_2\}$ $-(r_0^{\mathrm{H}} - q_0^{\mathrm{H}}) + 3a_1q_1^{\mathrm{H}}/4a_2 + q_2^{\mathrm{H}}/3a_2$	$s_4^{\mathrm{H}}/10^5\ \mathrm{cm}^{-1}$	1.62(77)	1.32
$r_{1q}^{\mathrm{H}} (= \tilde{r}_1^{\mathrm{H}}) = r_1^{\mathrm{H}} + (r_0^{\mathrm{H}} - q_0^{\mathrm{H}})$	q_0^{H}	-0.235(13)	
$r_{1q}^{\mathrm{Li}} (= \tilde{r}_1^{\mathrm{Li}}) = r_1^{\mathrm{Li}} + (r_0^{\mathrm{Li}} - q_0^{\mathrm{Li}})$	q_0^{Li}	0.564(70)	
$r_{2q}^{\mathrm{H}} (= \tilde{r}_2^{\mathrm{H}}) = r_2^{\mathrm{H}} - (r_0^{\mathrm{H}} - q_0^{\mathrm{H}}) - q_1^{\mathrm{H}}/2$	q_1^{H}	0.21(58)	
$r_{2q}^{\mathrm{Li}} (= \tilde{r}_2^{\mathrm{Li}}) = r_2^{\mathrm{Li}} - (r_0^{\mathrm{Li}} - q_0^{\mathrm{Li}}) - q_1^{\mathrm{Li}}/2$	q_1^{Li}	0.24(76)	
$r_{3q}^{\mathrm{H}} (= \tilde{r}_3^{\mathrm{H}}) = r_3^{\mathrm{H}} + (r_0^{\mathrm{H}} - q_0^{\mathrm{H}}) + q_1^{\mathrm{H}}/2 - q_2^{\mathrm{H}}/3$	q_2^{H}	-2.0(21)	

Fixed Parameters[c]**:**

$r_0^{\mathrm{H}} = -0.754\ 601\ 3(17)$ $r_1^{\mathrm{H}} = 1.259\ 149(23)$ $r_2^{\mathrm{H}} = -2.443\ 91(27)$ $r_3^{\mathrm{H}} = 4.097\ 18(96)$

$r_0^{\mathrm{Li}} = 0.774\ 280\ 9(20)$ $r_1^{\mathrm{Li}} = 0.597\ 152(27)$ $r_2^{\mathrm{Li}} = -1.486\ 70(32)$

[a] $\langle 0\,|L_x^2 + L_y^2\,|\,0\rangle = 2.18(h/2\pi)^2$ is assumed and a relation $s_i^{\mathrm{H}} = s_i^{\mathrm{Li}}$ is applied after Ref. (*41*).

[b] The uncertainty estimated by the error propagation.

[c] See text.

all three coefficients, q_i, r_i, and s_i, using $g_J(r_e)$ and a dipole moment function (*25*) is similarly impracticable because constraints obtained from only the dipole moment function do not affect the inner structure of optimal fitting parameters, or in other words, Watson's $\tilde{R}_{\mathrm{a,b}}$ and $\tilde{S}_{\mathrm{a,b}}$. An additional relation for electric dipolar moment (*22*),

$$\frac{d}{d\xi}M(\xi) = (er_e/2)\sum_{i=1}(q_i^{\mathrm{b}} - q_i^{\mathrm{a}})\xi^i, \qquad [54]$$

provides constraints between optimal fitting parameters $r_{i\mathrm{q}}^{\mathrm{a}}(= \tilde{r}_i^{\mathrm{a}})$ and $r_{i\mathrm{q}}^{\mathrm{b}}$ for *i* = 1, 2, ...:

$$r_{i\mathrm{q}}^{\mathrm{a}} = r_{i\mathrm{q}}^{\mathrm{b}}. \qquad [55]$$

Table 1 shows that experimental values of $r_{1\mathrm{q}}^{\mathrm{H}}$ and $r_{2\mathrm{q}}^{\mathrm{H}}$ are nearly equal to those of $r_{1\mathrm{q}}^{\mathrm{Li}}$ and $r_{2\mathrm{q}}^{\mathrm{Li}}$, respectively, within experimental errors.

Adiabatic and nonadiabatic expansion coefficients evaluated from parameters in Table 1 are listed in Table 2. This is the first estimate of adiabatic and non-adiabatic expansion coefficients made on the basis of detailed consideration of the experimental determinacy of coefficients based on Watson's $\tilde{R}_{\mathrm{a,b}}$ and $\tilde{S}_{\mathrm{a,b}}$. Fixed parameters $r_0^{\mathrm{H,Li}}$, $r_1^{\mathrm{H,Li}}$, $r_2^{\mathrm{H,Li}}$, and r_3^{H}, listed in Table 2 are obtained from accurate functions for $g_J(\xi)$ and dipolar moment given by Ogilvie *et al.* (*8, 21*) with Eqs. [52] and [53].

Adiabatic functions $S_{\mathrm{a,b}}(\xi)(s_i^{\mathrm{a,b}}, i = 1, 2, 3,$ and 4) for LiH agree well simply with those given by wobble–stretch theory (*1, 10, 41*). If we assume, in the wobble–stretch theory, that $\langle 0\,|\,L_x^2 + L_y^2\,|\,0\rangle$ is independent of *r* and of isotopic substitution (*1*), Watson's expression for $S_{\mathrm{a,b}}(r)$ (*1*) yields

$$\begin{aligned} S_{\mathrm{H}}(\xi) &= s_0^{\mathrm{H}} + s_1^{\mathrm{H}}\xi + s_2^{\mathrm{H}}\xi^2 + s_3^{\mathrm{H}}\xi^3 + \cdots \\ &\sim S_{\mathrm{Li}}(\xi) \\ &\sim \{\langle 0\,|\,L_x^2 + L_y^2\,|\,0\rangle/(2m_e r_e^2)\} \\ &\quad \times (1 - 2\xi + 3\xi^2 - 4\xi^3 + \cdots). \end{aligned} \qquad [56]$$

In Table 2, values of $s_1^{\mathrm{H,Li}}$, $s_2^{\mathrm{H,Li}}$, s_3^{H}, and s_4^{H} calculated with Eq. [56] and

$$\langle 0\,|\,L_x^2 + L_y^2\,|\,0\rangle\{= L(L+1)(h/2\pi)^2\} = 2.18(h/2\pi)^2, \quad [57]$$

are listed. The value of the matrix element is near that for $L = 1$. Although the wobble–stretch theory provides a rough estimate with an assumption of $s_i^{\mathrm{H}} = s_i^{\mathrm{Li}}$, the sign and magnitude of experimental values of the expansion coefficients of $S_{\mathrm{H,Li}}(\xi)$ are reproduced well with this theory.

We ignore $s_0^{\mathrm{H,Li}}$ from Eq. [5] because these terms do not participate in spectral transitions within one electronic state. However, if the wobble–stretch theory is assumed to be applicable, a value of $s_0^{\rm H} = s_0^{\rm Li}$ is estimated to be ∼0.264 from Eq. [56]. Extended determinations of $S_{\rm a,b}(\xi)$, using the present method for other molecules will provide useful understanding of the adiabatic functions $S_{\rm a,b}(\xi)$.

An estimate of the vibrational g factor

$$g_v(\xi = 0) = (m_{\rm p}/M_{\rm H})q_0^{\rm H} + (m_{\rm p}/M_{\rm Li})q_0^{\rm Li} \qquad [58]$$

is −0.154(16) for ^{7}LiH (*22*). Values of $B_{\rm e}$, $r_{\rm e}$, $\omega_{\rm e}$, and k from the present fit are 7.520 214 0(20) cm^{-1}, 1.594 911 3(11)$\times 10^{-10}$ m, 1 406. 079 2(12) cm^{-1}, and 102.651 05(11) Nm^{-1}, respectively, for ^{7}LiH.

APPENDIX

Equation [12] is written as

$$\frac{d^2\psi}{d\eta^2} + \frac{1}{B'_{\rm e}}(F_{vJ} - U_J)\psi = 0 \qquad [A.59]$$

and

$$\begin{aligned} U_J &= (\omega_{\rm e}^2/4B_{\rm e})(1+g_3)\eta^2\left(1+\sum_{i=1} k_i\eta^i\right) + B_{\rm e}(1+g_2) \\ &\quad \times \left(1+\sum_{i=1} r'_i\eta^i\right)(1+\eta)^{-2}J(J+1) \\ &= k_0\eta^2(1+k_1\eta+k_2\eta^2+\cdots) + B_{\rm e}^*J(J+1)\{1-2 \\ &\quad \times(1-\delta r'_1/2)\eta + 3(1-2\delta r'_1/3+\delta r'_2/3)\eta^2 - \cdots\}, \qquad [A.60] \end{aligned}$$

in which $B_{\rm e}^* = B_{\rm e}(1+g_2)$, $B'_{\rm e} = B_{\rm e}(1+g_1) = B_{\rm e}^*(1-\delta r'_0)$ and all quantities involving the energy are in cm^{-1} : E_{vJ} of Eq. [12] is replaced by hcF_{vJ} and $B_{\rm e}[= h/(8\pi^2 c\mu r_{\rm e}^2)]$, $\omega_{\rm e}[= (1/2\pi c)(k/\mu)^{1/2}]$, and $\delta s'_i$ are in cm^{-1}.

A variable ρ such that $\eta = \rho + \varepsilon$ is introduced, where ε is so chosen that the minimum of U_J falls to the point $\rho = 0$. According to Dunham (*17*) and Kilpatrick (*27*) the displacement ε can be expressed as

$$\varepsilon = \sum_{i=1} \varepsilon_i\left\{\left(B_{\rm e}^*/\omega_{\rm e}^*\right)^2 J(J+1)\right\}^i, \qquad [A.61]$$

in which the magnitude of each term on the right side of Eq. [A.61], $\varepsilon_i\{(B_{\rm e}^*/\omega_{\rm e}^*)^2J(J+1)\}^i$, decreases successively with $i(=1, 2, 3, \ldots)$ to a proportional factor $(B_{\rm e}/\omega_{\rm e})^2$. Coefficients ε_i are determined with the condition that

$$\left(\frac{dU_J}{d\rho}\right)_{\rho=0} = 0 \qquad [A.62]$$

and the fact that the quantum number J can take arbitrary numbers. Then, as has been shown by Dunham (*17*), the potential U_J is expressed as a power series in ρ of the same form as Eq. [2],

$$U_J = \kappa_0^J\rho^2\left(1 + k_1^J\rho + k_2^J\rho^2 + \cdots\right) + U_0^J. \qquad [A.63]$$

Quantities with a superscript J in Eq. [A.63] are those expressed in polynomials of $J(J+1)$.

By use of Dunham's result (*16*, *17*), which has also been derived with perturbation theory, the eigenvalue F_{vJ} in Eq. [A.59] can be obtained through

$$\begin{aligned} F' &= B'_{\rm e}A'_1A'_3/16 + A'_1B_{\rm e}^{\prime 1/2}(v+1/2) + \left(B_{\rm e}^{\prime 3/2}A_1^{\prime 2}/32\right) \\ &\quad \times(5A'_5 - B'_2A'_3)(v+1/2) - (B'_{\rm e}B'_2A_1^{\prime 2}/4)(v+1/2)^2 \\ &\quad + \left(B_{\rm e}^{\prime 2}A_1^{\prime 3}/128\right)\left(35A'_7 - 15B'_2A'_5 + 3A'_3B_2^{\prime 2} - 3A'_3B'_4\right) \\ &\quad \times(v+1/2)^2 + (B_{\rm e}^{\prime 3/2}A_1^{\prime 3}/8)(B_2^{\prime 2} - B'_4)(v+1/2)^3 \\ &\quad + \left(B_{\rm e}^{\prime 2}A_1^{\prime 4}/64\right)\left(10B'_2B'_4 - 5B_2^{\prime 3} - 5B'_6\right) \\ &\quad \times(v+1/2)^4 + \cdots, \qquad [A.64] \end{aligned}$$

in which

$$F' = F_{vJ} - U_0^J, \qquad [A.65]$$

$$A'_1 = 2\kappa_0^{J1/2}; \quad A'_2 = 2k_1^J; \ldots; \text{ etc.}, \qquad [A.66]$$

$$B'_2 = \left(1/2\kappa_0^J\right)\left(15k_1^{J2}/4 - 3k_2^J\right); \ldots; \text{ etc.} \qquad [A.67]$$

Equation [A.64] is the same as that given by Dunham except that a symbol ′ is here attached to all quantities. A misprint in Dunham's original equation was corrected in Ref. (*18*). $B'_{\rm e}$ is defined in Eq. [A.59], and a symbol ′ for other quantities means that those given by Dunham were slightly corrected according to Eqs. [A.66] and [A.67]. The above calculation yields vibrational–rotational energy F_{vJ}.

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