

# Improved Parameterization for Combined Isotopomer Analysis of Diatomic Spectra and Its Application to HF and DF

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A new way of representing vibration–rotation term values for multiple isotopomers of a given electronic state of a diatomic molecule is presented which resolves problems associated with the way the conventional combined isotopomer expansion represents the atomic mass-dependent JWKB and Born–Oppenheimer breakdown correction terms. Its application to infrared and microwave data for HF and DF yields new Dunham expansion coefficients and Born–Oppenheimer breakdown correction terms for this species. This procedure is implemented in a generally available computer program for fitting to various types of data involving one or several electronic states of multiple isotopomers of a diatomic molecule. © 1999 Academic Press

## I. INTRODUCTION

Transition frequencies for isotopomer  $\alpha$  of a diatomic molecule in a  $^1\Sigma$  electronic state are commonly represented by differences between vibration–rotation level energies represented either by “band constant” expressions

$$E_{BC}^\alpha(\nu, J) = G^\alpha(\nu) + B_v^\alpha[J(J+1)] - D_v^\alpha[J(J+1)]^2 + H_v^\alpha[J(J+1)]^3 + \dots \equiv \sum_m K_m^\alpha(\nu)[J(J+1)]^m \quad [1]$$

or by Dunham expansions

$$E_{\text{Dun}}^\alpha(\nu, J) = \sum_{l,m} Y_{l,m}^\alpha(\nu + \frac{1}{2})[J(J+1)]^m, \quad [2]$$

in which  $\nu$  and  $J$  are the usual vibrational and rotational quantum numbers (1–3). In the simplest treatments, independent sets of constants are obtained for each isotopomer,  $\alpha$ . However, this involves considerable redundancy, since the resulting constants for different isotopomers are known to be interrelated. For instance, if one overlooks their vibrational dependence,  $m > 0$  (rotational) band constants for isotopomers  $\alpha$  and  $\beta$  of a given species obey the approximate relationship  $K_m^\beta = K_m^\alpha(\mu_\alpha/\mu_\beta)^m$ , where  $\mu_\alpha = M_A^\alpha M_B^\alpha / (M_A^\alpha + M_B^\alpha)$  is the usual reduced mass of isotopomer  $\alpha$  of a molecule formed from atoms  $A$  and  $B$  with atomic masses  $M_A^\alpha$  and  $M_B^\alpha$ , respectively. Similarly, subject to the two approximations that (i) different isotopomers experience exactly the same effective internuclear potential energy function, and (ii) the first-order JWKB approximation or Bohr–Sommerfeld quantization con-

dition is exact, the Dunham coefficients for different isotopomers of the same species obey the simple semiclassical scaling relationship (1–3)

$$Y_{l,m}^\beta = Y_{l,m}^\alpha(\mu_\alpha/\mu_\beta)^{m+l/2}. \quad [3]$$

The fact that these two conditions are never exactly valid has stimulated a search for a better way of representing results for multiple isotopomers of a given species.

It has long been known that within the higher order JWKB approximation, the leading corrections to the Dunham coefficients  $Y_{l,m}^\alpha$  scale as  $(1/\mu_\alpha)$  (1, 2, 4). Moreover, the leading corrections to the interaction potential between atoms  $A$  and  $B$  due to the partial breakdown of the Born–Oppenheimer approximation have been shown to scale as  $1/M_A$  and  $1/M_B$  (5–9). These considerations led Ross *et al.* (10) to introduce the general multi-isotopomer Dunham-type level energy expression (where  $m_e$  is the mass of the electron):

$$E^\alpha(\nu, J) = \sum_{l,m} \frac{U_{l,m}}{(\mu_\alpha)^{m+l/2}} \left( 1 + \frac{m_e}{M_A^\alpha} \Delta_{l,m}^A + \frac{m_e}{M_B^\alpha} \Delta_{l,m}^B \right) \times (\nu + \frac{1}{2})^l [J(J+1)]^m, \quad [4]$$

for which Bunker (8) and Watson (9) later provided theoretical justification. This expression is widely used and seems to be generally accepted as the best way to provide a single unified representation of vibration–rotation level energies for multiple isotopomers of the same species. However, problems with the form of this expansion pointed out by Watson (9) and Tiemann (11), together with a number of other deficiencies noted below,

stimulated the present proposal for an improved representation of the atomic mass-dependent corrections.

## II. SHORTCOMINGS OF THE CONVENTIONAL DESCRIPTION OF MASS-DEPENDENT DIATOM LEVEL ENERGY CORRECTIONS

Problems associated with the use of Eq. [4] include the following.

1. The coefficients  $\{U_{l,m}\}$ , which effectively supplant the familiar Dunham constants  $\{Y_{l,m}\}$ , have units which depend on fractional powers of mass and vary from one term to another.

2. Except for hydrides with masses expressed in atomic mass units, the magnitudes of the  $\{U_{l,m}\}$  parameters are not even qualitatively similar to those of the familiar  $\{Y_{l,m}\}$  constants for normal isotopic forms of those systems, and they are not simply related to observed level spacings. Moreover, since the  $\{U_{l,m}\}$  effectively represent how the level energies would behave if the first-order JWKB approximation was exact and if Born–Oppenheimer breakdown corrections were identically zero, they describe a hypothetical limiting situation, making their physical significance somewhat obscure.

3. The term value expression of Eq. [4] involves products of  $U_{l,m}$  with  $\Delta_{l,m}^A$  and  $\Delta_{l,m}^B$ , so determining proper statistical uncertainties in fitted values of these constants necessarily requires the use of either iterative nonlinear fits or indirect methods.

4. Because their contributions to the level energies depend on their products with the  $U_{l,m}$  coefficients, the magnitudes of the dimensionless parameters  $\Delta_{l,m}^A$  and  $\Delta_{l,m}^B$  alone provide no direct indication of the magnitudes of the associated corrections to those energies, since (as pointed out by Watson (9)) an accidental anomalously small/large  $U_{l,m}$  will tend to give rise to anomalously large/small  $\Delta_{l,m}^A$  and  $\Delta_{l,m}^B$  values.

5. The treatment of the  $(l, m) = (0, 0)$  term is unsatisfactory. Since the factors  $U_{l,m}/(\mu_\alpha)^{m+1/2}$  are what the isotopic  $Y_{l,m}^\alpha$  coefficients would be if the first-order JWKB approximation was exact and if the intermolecular potential function was identical for all isotopomers, necessarily  $U_{0,0} \equiv 0$ . Because these conditions are never exactly satisfied, the product terms  $U_{0,0}\Delta_{0,0}^A$  and  $U_{0,0}\Delta_{0,0}^B$  associated with the conventional Dunham  $Y_{0,0}$  term are in general nonzero, which implies that the associated  $\Delta_{0,0}^A$  and  $\Delta_{0,0}^B$  coefficients are infinite.

6. Since the coefficients  $\Delta_{l,m}^A$  and  $\Delta_{l,m}^B$  appear as multiplicative correction factors in a Dunham-like expansion, this formulation is incompatible with the use of non-Dunham expressions for vibrational energies and rotational constants. In particular, it is well known that power series in  $(v + \frac{1}{2})$  behave very poorly when one attempts to use them to represent levels ranging to very high energies. On the other hand, “near-dissociation expansions” explicitly incorporate the theoretic-

cally known limiting behavior of vibrational energies and rotational constants near the dissociation limit and can very efficiently represent data for levels extending all the way down to the potential minimum (12–15). However, there is no way to incorporate the multiplicative Ross *et al.* (10) description of these atomic mass-dependent correction terms into near dissociation expansion level energy expressions. Thus, Eq. [4] is unsuitable for representing the energies of levels spanning the entire potential energy well.

7. Fits cannot yield  $U_{l,m}$ 's truly independent of mass unless data are available for isotopomers formed from more than one isotope of *both* of the atoms forming the molecule. As a result, although formally mass independent, fitted values of  $\{U_{l,m}\}$  parameters actually depend on the isotopic range of the data available for analysis and would change as data for additional isotopomers became available. For example,  $\{U_{l,m}\}$  coefficients obtained from a combined isotope fit of data for  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  to Eq. [4] would be effective values, contaminated by contributions from the  $\Delta_{l,m}^H$  terms, and truly mass-independent  $U_{l,m}$ 's would not be obtained unless data for  $\text{D}^{35}\text{Cl}$  and/or  $\text{D}^{37}\text{Cl}$  were also included in the analysis.

8. For most systems, one isotopomer is usually of dominant abundance, and experimental data available for minority forms tend to be fragmentary or to span a relatively restricted range of energy. As a result, the range of energies over which the corrections determined by the  $\Delta_{l,m}^A$  and  $\Delta_{l,m}^B$  coefficients are defined is generally much more limited than that associated with the data for the dominant isotopomer. Since the idealized energies defined by the  $U_{l,m}$  coefficients are effectively determined by *subtracting* these correction terms from the results for the dominant isotopomer, energies defined by the  $U_{l,m}$ 's alone are necessarily relatively poorly defined beyond the range of data for the *least* well defined of the minority isotopomers which determined the  $\{\Delta_{l,m}\}$  correction coefficients.

9. Tiemann and co-workers have shown that for molecules formed from heavy nuclei, the leading Born–Oppenheimer breakdown corrections are not the inverse mass-scaled corrections represented by the  $\Delta_{l,m}^{A,B}$  terms in Eq. [4], but rather are “field shift” corrections due to finite nuclear size, which scale as the mean square radius of the nucleus charge,  $\langle r^2 \rangle_A$  (16–18). Because absolute values of  $\langle r^2 \rangle_A$  are much less accurately known than the differences between them for diverse isotopes of a given species (18, 19), taking account of such effects requires that a particular molecular isotopomer be selected as a reference point, rather than the hypothetical limiting case associated with the  $U_{l,m}$  constants of Eq. [4].

While the concerns listed above are of varying levels of importance, there are clearly significant difficulties associated with the use of Eq. [4]. However, a relatively straightforward rearrangement of the terms appearing there resolves all of these difficulties.

### III. IMPROVED DESCRIPTION OF ATOMIC MASS-DEPENDENT CORRECTIONS IN DIATOM LEVEL ENERGY EXPRESSIONS

The revised formulation recommended here is based on two key requirements. The first is that the atomic mass-dependent correction terms should be additive, rather than multiplicative, and the second is that the properties of a selected dominant isotopomer should be used as the reference point for these corrections, rather than the extrapolated nonphysical limiting case in which the first-order JWKB approximation is assumed to be exact and atomic mass-dependent potential energy function corrections are ignored. Converting Eq. [4] to the new form may be thought of as consisting of two steps.

(i) Multiply through by  $U_{l,m}$  and separate Eq. [4] into two expansions, one involving only the  $U_{l,m}$  coefficients, and one containing all the atomic mass-dependent correction terms. The first expansion would include only terms with  $(l, m) \neq (0, 0)$ , while the second begins with the  $(l, m) = (0, 0)$  term.

(ii) Select as the reference species the dominant isotopomer ( $\alpha = 1$ ), for which precise data are available over the broadest range of energies, and rewrite the terms dependent on atomic masses as corrections to energies obtained on applying simple first-order semiclassical quantum number mass scaling to the actual level energy expression for isotopomer  $\alpha = 1$ . This involves collecting and rearranging the sums of Eq [4], but introduces no new terms.

Applying these steps to Eq. [4] yields the present recommended multi-isotopomer generalization of the Dunham level energy expansion:

$$E^\alpha(v, J) = \sum_{(l,m) \neq (0,0)} Y_{l,m}^1 \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} \left( v + \frac{1}{2} \right)^l [J(J+1)]^m + \sum_{(l,m) \neq (0,0)} \left\{ \frac{\Delta M_A^\alpha}{M_A^\alpha} \delta_{l,m}^A + \frac{\Delta M_B^\alpha}{M_B^\alpha} \delta_{l,m}^B \right\} \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} [5] \times \left( v + \frac{1}{2} \right)^l [J(J+1)]^m,$$

where  $\Delta M_A^\alpha = M_A^\alpha - M_A^1$ , and  $\alpha = 1$  identifies the select reference isotopomer. This expression is formally equivalent to Eq. [4] because

$$\Delta_{l,m}^A = -\delta_{l,m}^A M_A^1 (\mu_1)^{m+l/2} / U_{l,m} m_e \quad [6]$$

and

$$U_{l,m} = (\mu_1)^{m+l/2} (Y_{l,m}^1 + \delta_{l,m}^A + \delta_{l,m}^B), \quad [7]$$

while Dunham coefficients for other ( $\alpha \neq 1$ ) isotopomers are readily generated from

$$Y_{l,m}^\alpha = \left\{ Y_{l,m}^1 + \frac{\Delta M_A^\alpha}{M_A^\alpha} \delta_{l,m}^A + \frac{\Delta M_B^\alpha}{M_B^\alpha} \delta_{l,m}^B \right\} \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+l/2}. \quad [8]$$

The use of Eq. [5] in fits to experimental data resolves all of the problems listed in Section II, particularly as follows.

1. All of the coefficients  $\{Y_{l,m}^1\}$ ,  $\{\delta_{l,m}^A\}$ , and  $\{\delta_{l,m}^B\}$  appearing in Eq. [5] have units  $\text{cm}^{-1}$ .

2. The expansion coefficients for the reference isotopomer  $\{Y_{l,m}^1\}$  are the familiar Dunham expansion coefficients of isotopomer 1, and hence, have the usual magnitudes and significance. The conventional Dunham coefficients for other isotopomers are readily generated from Eq. [8].

3. Since the mass-dependent correction terms are now additive, the  $\{\delta_{l,m}^A\}$  and  $\{\delta_{l,m}^B\}$  coefficients, and their uncertainties, may be determined directly in linear least-squares fits.

4. The magnitudes of the  $\{\delta_{l,m}^A\}$  and  $\{\delta_{l,m}^B\}$  coefficients are a relatively direct measure of the magnitude of the JWKB and Born–Oppenheimer breakdown energy corrections. The numerical values of these coefficients are isotopomer independent for a given system, although they do depend on the choice of the reference isotopomer (see Eq. [6]). There should be no ambiguity, however, because of the standard convention that the reference isotopomer is the one based on the most abundant isotope of each atom (20). In the rare cases when one might wish to change the choice of reference isotopomer, the conversion is straightforward:

$$\delta_{l,m}^A(2) = \delta_{l,m}^A(1) (M_A^1/M_A^2) (\mu_1/\mu_2)^{m+l/2}. \quad [9]$$

5. The separation into two expansions allows a straightforward treatment of the  $(l, m) = (0, 0)$  terms.

6. If non-Dunham expressions (such as near-dissociation expansions (12–15) are used for the vibration–rotation energies of the reference isotopomer  $\alpha = 1$ , the vibrational and rotational quantum numbers in the expansions for the reference species ( $\alpha = 1$ ) are simply replaced by the first-order semi-classically scaled quantities:

$$\left( v + \frac{1}{2} \right) \rightarrow \sqrt{\mu_1/\mu_\alpha} \left( v + \frac{1}{2} \right) \quad \text{and} \quad [10] \\ [J(J+1)] \rightarrow (\mu_1/\mu_\alpha) [J(J+1)],$$

while the treatment of the mass-dependent correction terms and the values of the associated corrections coefficients  $\{\delta_{l,m}^A\}$  and

$\{\delta_{l,m}^B\}$  would not change. The resulting generalization of Eq. [5] may be written as

$$E^\alpha(v + \frac{1}{2}, [J(J+1)]) = E^1(\sqrt{\mu_1/\mu_\alpha}(v + \frac{1}{2}), (\mu_1/\mu_\alpha)[J(J+1)]) + \sum_{(l,m) \geq (0,0)} \left\{ \frac{\Delta M_A^\alpha}{M_A^\alpha} \delta_{l,m}^A + \frac{\Delta M_B^\alpha}{M_B^\alpha} \delta_{l,m}^B \right\} \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+l/2} (v + \frac{1}{2})^l [J(J+1)]^m. \quad [11]$$

For near-dissociation expansions, this means that the independent variable in the expressions for the band constants  $K_m^\alpha(v)$  for isotopomer  $\alpha$  becomes  $\sqrt{\mu_1/\mu_\alpha}(v_{\infty} - v)$ .

7. Once the reference isotopomer is chosen and its data are fitted, inclusion of data for other isotopomers allows the determination of  $\{\delta_{l,m}^A\}$  and/or  $\{\delta_{l,m}^B\}$  coefficients, but should have no effect on the fitted  $\{Y_{l,m}^1\}$  values, other than what might be expected from the improved statistics associated with inclusion of more data in the fit. For example, if an analysis initially treated data for  $\text{H}^{35}\text{Cl}$  alone, subsequent inclusion of data for  $\text{H}^{37}\text{Cl}$  then  $\text{D}^{35}\text{Cl}$  and/or  $\text{D}^{37}\text{Cl}$  should lead to little significant change in the initially determined  $\{Y_{l,m}^1\}$  values. This would *not* be the case for the  $\{U_{l,m}\}$  coefficients of Eq. [4].

8. The fact that data for minority isotopomers is sparse or spans a relatively limited range should not affect the uncertainties in either the  $Y_{l,m}^1$ 's for the reference isotopomer or the energies predicted from them.

9. The use of a dominant isotopomer as the reference species facilitates the inclusion of the correction terms due to finite nuclear size, as discussed by Tiemann and co-workers (16–18). In this case, the correction terms in Eqs. [5] or [11] would be augmented to include contributions to take account of the different isotopic nuclear charge radii:

$$\left\{ \delta \langle r^2 \rangle_A^\alpha f_{l,m}^A + \delta \langle r^2 \rangle_B^\alpha f_{l,m}^B + \frac{\Delta M_A^\alpha}{M_A^\alpha} \delta_{l,m}^A + \frac{\Delta M_B^\alpha}{M_B^\alpha} \delta_{l,m}^B \right\}, \quad [12]$$

where  $\delta \langle r^2 \rangle_A^\alpha$  is the known (19) difference between the values of the mean-square nuclear charged radii  $\langle r^2 \rangle_A$  of atom  $A$  in the reference isotopomer and in isotopomer  $\alpha$ , and  $f_{l,m}^A$  and  $f_{l,m}^B$  are field effect expansion coefficients analogous to the  $\delta_{l,m}^A$  and  $\delta_{l,m}^B$  values. Note that while the  $\langle r^2 \rangle_A$  values have a different dependence on nuclear size than does the mass  $M_A$  (16, 18), empirically distinguishing between these terms requires accurate data for molecules formed from at least three different isotopes of the atom in question.

#### IV. ILLUSTRATIVE APPLICATION TO HF AND DF

A computer program with the ability to fit any combination of appropriately weighted microwave, infrared, electronic band, and fluorescence data for multiple isotopomers to either Eq. [5], if a Dunham expansion is used to describe the reference isotopomer, or to a version of Eq. [11] if near-dissociation expansions are used, may be obtained from the author on request.<sup>1</sup> This program incorporates a “sequential rounding and refitting” (SRR) procedure for minimizing the numbers of significant digits which must be reported for fitted parameters without loss of accuracy, as described in Ref. (21). The masses of all stable atomic isotopes, taken from the 1993 mass table (22), are incorporated in a data subroutine in the program.

As an illustrative application, the present approach has been applied to a recent compendium of high-quality infrared and microwave data for HF and DF. Ram *et al.* (23) reported extensive new infrared emission spectra for HF and DF and combined those data with complementary earlier IR data and the best existing microwave measurements in least-squares fits which yielded optimal band constants  $\{G_v, B_v, D_v, \text{etc.}\}$  for levels  $v = 0-5$  of both isotopomers. While electronic spectra provide lower resolution data for the higher vibrational levels of this system (24, 25), the present analysis was restricted to the data set of Ref. (23) in order to facilitate comparisons with conventional methods of analysis.

Table 1 presents results obtained on fitting the HF and DF data of Ref. (23), weighted by the inverse squares of their uncertainties, to the generalized Dunham-type expansion of Eq. [5]. Its first column shows the results of a fit to the HF data alone; these are identical to the SRR results in the last column of Table 1 in Ref. (21). The second column then shows the results of a simultaneous fit of Eq. [5] to the data for both HF and DF. They provide the most compact and accurate set of Dunham-type constants for the lower levels of ground state HF and DF. As expected, the values of the  $\{Y_{l,m}^{\text{HF}}\}$  constants are very similar in the two fits, in most cases agreeing within their mutual uncertainties, with those obtained from the two-isotopomer fit having the smaller uncertainties expected for a larger data set. Thus, as predicted in point number 7 in the previous section, the fitted parameters for the reference isotopomer are not significantly affected by inclusion of the results for the second (minority) isotopomer. In both of these sets of results, the numbers of significant digits required to represent the parameters with no loss of precision in their representation of the data was minimized by the SRR procedure of Ref. (21) incorporated in program “DSParFit.”

The third column of results in Table 1 presents the parameters for DF generated from the results in the second column using Eq. [8]; they are rounded at the first significant digit of the “parameter sensitivity” (21). These parameter values require more significant

<sup>1</sup> Requests for this program “DSParFit” (Diatomic Singlet Parameter Fits) should be sent by electronic mail to leroy@UWaterloo.ca.

TABLE 1  
Parameters for *X* State HF and DF (in  $\text{cm}^{-1}$ ) Obtained on Fitting Eq. [5] to the Data of Ref. (23)

<i>constant</i>	HF constants determined from fits to:		DF constants determined from:	
	HF data alone	HF and DF data	HF/DF fit constants <sup>a</sup>	DF data alone
$Y_{1,0}$	4138.38707 (270)	4138.38503 (140)	3000.0817682 (9000)	3000.0801 (15)
$Y_{2,0}$	-89.94511 (280)	-89.94319 (140)	-47.271154 (710)	-47.2696 (15)
$Y_{3,0}$	0.92521 (120)	0.924488 (610)	0.35205062 (23000)	0.351462 (630)
$Y_{4,0}$	-0.015613 (230)	-0.015495 (120)	-0.004279808 (32000)	-0.004181 (120)
$Y_{5,0}$	-0.000432 (15)	-0.000439 (8)	-0.0000879033 (16000)	-0.000094 (8)
$Y_{0,1}$	20.9537256 (74)	20.953712 (4)	11.01069698 (200)	11.0106903 (16)
$Y_{1,1}$	-0.7934125 (240)	-0.7933704 (130)	-0.302202795 (4500)	-0.3021824 (45)
$Y_{2,1}$	0.0109622 (220)	0.0109244 (120)	0.003015726 (3300)	0.0029983 (33)
$10^4 Y_{3,1}$	-2.3314 (850)	-2.1929 (480)	-0.4390962 (95000)	-0.3787 (80)
$10^4 Y_{4,1}$	-0.01 (1)	-0.032 (8)	-0.0046451 (12000)	-0.0139 (6)
$10^4 Y_{5,1}$	-0.00614 (88)	-0.00488 (54)	-0.00051354 (5700)	-
$10^4 Y_{0,2}$	-21.48964 (43)	-21.489118 (270)	-5.9327817 (740)	-5.93258 (7)
$10^4 Y_{1,2}$	0.58593 (56)	0.585174 (370)	0.1170465 (700)	0.116707 (72)
$10^8 Y_{2,2}$	-115.4 (36)	-110.71 (240)	-16.07074 (35000)	-14.15 (37)
$10^8 Y_{3,2}$	-1.6 (9)	-2.8 (6)	-0.29466 (6600)	-0.72 (5)
$10^8 Y_{4,2}$	-0.535 (76)	-0.434 (54)	-0.03311 (410)	-
$10^8 Y_{0,3}$	16.6133 (160)	16.5981 (100)	2.408014 (1500)	2.40401 (110)
$10^8 Y_{1,3}$	-0.4685 (85)	-0.4606 (62)	-0.0481554 (6400)	-0.0444 (6)
$10^8 Y_{2,3}$	-0.003 (3)	-0.005 (2)	-0.00038145 (16000)	-0.0016 (1)
$10^8 Y_{3,3}$	-0.00258 (33)	-0.00234 (26)	-0.00012942 (1400)	-
$10^{12} Y_{0,4}$	-15.635 (260)	-15.402 (180)	-1.175012 (14000)	-1.1419 (64)
$10^{12} Y_{1,4}$	0.32 (7)	0.26 (6)	0.0143796 (30000)	-0.003 (2)
$10^{12} Y_{2,4}$	-0.063 (8)	-0.059 (6)	-0.0023656 (2600)	-
$10^{16} Y_{0,5}$	15. (2)	13.4 (14)	0.537262 (54000)	0.42 (1)
$10^{16} Y_{1,5}$	-1.17 (23)	-0.98 (18)	-0.028485 (5400)	-
$10^{20} Y_{0,6}$	-11. (5)	-7. (4)	-0.1475 (810)	-
$\delta_{1,0}^H$	-	-0.1139 (8)	-	-
$\delta_{2,0}^H$	-	-0.0048 (5)	-	-
$\delta_{3,0}^H$	-	-0.00094 (8)	-	-
$10^3 \delta_{0,1}^H$	-	-6.035 (4)	-	-
$10^3 \delta_{1,1}^H$	-	0.373 (6)	-	-
$10^3 \delta_{2,1}^H$	-	-0.012 (1)	-	-
$10^6 \delta_{0,2}^H$	-	1.91 (2)	-	-
$10^6 \delta_{1,2}^H$	-	-0.126 (19)	-	-
$10^{10} \delta_{0,3}^H$	-	-1.9 (2)	-	-
$10^{10} \delta_{1,3}^H$	-	0.6 (2)	-	-
<i>No. of data</i>	326	722	396	396
<i>No. parameters</i>	26	36	0	20
$\bar{\sigma}_f$	0.930	0.877	0.792	0.780

Note. The numbers in parentheses are the 95% confidence limit uncertainties in the last significant digits shown.  
<sup>a</sup> Generated from Eq. [8] and the results in the preceding column, with uncertainties calculated as per Eq. [7] of Ref. (21).

digits to represent them adequately, as the compensating changes associated with the sequential rounding and refitting procedure do not come into play. Their (95% confidence limit) uncertainties are generated by normal error propagation techniques, as discussed in Section VI of Ref. (21).

The last column in Table 1 then lists parameters obtained from an independent fit to the data for DF alone. Relative to the results in the preceding column, fewer significant digits are generally required, as the SRR procedure can be applied. However, because

the DF data set is less extensive than that for HF, fewer well-defined constants are obtained, and the associated uncertainties are often larger. This occurs because in the combined fit the improved quality and range of the data for the dominant isotopomer (HF) are effectively propagated into the representation for the minority species (DF), yielding better defined parameters for the latter than can be obtained from a fit to its data alone. This will generally be true for the properties of minority isotopomers determined in a multi-isotopomer analysis.

## V. MASS-DEPENDENT CORRECTIONS TO ELECTRONIC AND CENTRIFUGAL POTENTIAL FUNCTIONS

Most spectroscopic analysis still consists of least-squares fits to parameterized level energy expressions such as Eqs. [1], [2], [4], [5], or [11]. However, for diatomic molecules it is becoming increasingly common to fit data directly to eigenvalue differences calculated numerically from the effective radial Schrödinger equation (26, 9)

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_{ad}^\alpha(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} \right. \\ \left. \times [1 + q^\alpha(R)] - E_{v,J} \right\} \psi_{v,J}(R) = 0, \quad [13]$$

where the effective radial potential for isotopomer  $\alpha$ ,  $V_{ad}^\alpha(R)$ , and the nonadiabatic centrifugal distortion correction term  $q^\alpha(R)$ , are represented by analytic functions, the parameters of which are the variables being fitted to.

A variety of ways of representing the atomic mass-dependent adiabatic potential correction function and (nonadiabatic) effective centrifugal distortion correction function  $q^\alpha(R)$  have been used in previous work (9, 27–30). However, most suffer from a number of the same deficiencies outlined in Section II. In particular, the mass-dependent corrections to the effective radial potential and centrifugal term are commonly expressed as

$$V_{ad}^\alpha(R) = V_{CN}(R) + \frac{1}{M_A^\alpha} \Delta V_A(R) + \frac{1}{M_B^\alpha} \Delta V_B(R) \quad [14]$$

and

$$q^\alpha(R) = \frac{1}{M_A^\alpha} \bar{q}_A(R) + \frac{1}{M_B^\alpha} \bar{q}_B(R), \quad [15]$$

where  $V_{CN}(R)$  is the “clamped nuclei” potential obtained within the Born–Oppenheimer approximation on neglecting the dependence of the electronic wavefunction on the internuclear distance,  $\Delta V_A$  and  $\Delta V_B$  are adiabatic corrections to the potential obtained as the expectation values of the terms in the electronic Hamiltonian involving radial derivatives of the electronic wavefunction, and  $\bar{q}_A(R)$  and  $\bar{q}_B(R)$  are the individual atomic contributions to the nonadiabatic centrifugal corrections (5–7, 31, 32). Alternate versions of these expressions explicitly incorporate the mass of the electron, making the factor in front of each correction term  $m_e/M_{A,B}^\alpha$ . This simplifies the units, but the strengths of the various correction functions still do not directly represent the magnitudes of those terms.

As with Eq. [4], Eqs. [14] and [15] give correction functions in inconvenient units involving the atomic mass (problem 1 in Section II), and the simple inverse-mass scaling makes the

magnitudes of the  $\bar{q}_A(R)$  and  $\bar{q}_B(R)$  functions inconvenient to compare with each other or from system to system (problem 4 in Section II). Moreover, the clamped nuclei limit is a non-physical situation which would be of direct interest only in the limited number of cases (such as  $\text{HeH}^+$  (33)) in which *ab initio* electronic structure calculations can be performed with sufficient accuracy to allow quantitative comparisons with these empirically determined functions. However, even for those systems, the empirical functions determined from spectroscopic data will be more accurate than the *ab initio* results, so such comparisons would have only qualitative significance.

Other problems from Section II also arise here. For example, in number 7, one’s estimate of the true  $V_{CN}(R)$  function will change as the range of isotopomeric data increases (see, e.g., Eq. (15) of Ref. (34)); as in number 8, uncertainties in the extrapolated adiabatic correction functions  $\Delta V_A(R)$  and  $\Delta V_B(R)$  at distances beyond the range of data for minority isotopomers introduce analogous uncertainties in  $V_{CN}(R)$ ; and as in number 9, a reference isotopomer is required if one is to use the known (19)  $\delta\langle r^2 \rangle_A^\alpha$  values to determine field-effect radial correction functions. Problem number 8 is exacerbated by the fact that much of the earlier work used power series in  $R$  to represent these correction functions (27–29), which means that the resulting effective radial potentials for all real physical isotopomers became singular (instead of approaching an asymptote) as  $R \rightarrow \infty$ .

All of the above problems are resolved if one follows the approach of Section III and selects as the reference species “. . . the dominant isotopomer ( $\alpha = 1$ ) for which precise data are available over the broadest range of energies,” and introduces appropriate mass scaling. Doing this converts Eqs. [14] and [15] to the forms

$$V_{ad}^\alpha(R) = V_{ad}^1(R) + \frac{\Delta M_A^\alpha}{M_A^1} \Delta V_{ad}^A(R) + \frac{\Delta M_B^\alpha}{M_B^1} \Delta V_{ad}^B(R) \quad [16]$$

and

$$q^\alpha(R) = \frac{M_A^1}{M_A^\alpha} q_A(R) + \frac{M_B^1}{M_B^\alpha} q_B(R), \quad [17]$$

where, as before,  $\Delta M_A^\alpha = M_A^\alpha - M_A^1$  and  $\Delta M_B^\alpha = M_B^\alpha - M_B^1$ , and of course,  $\Delta V_{ad}^A(R) = -\Delta V_A(R)/M_A^1$ ,  $\Delta V_{ad}^B(R) = -\Delta V_B(R)/M_B^1$ ,  $q_A(R) = \bar{q}_A(R)/M_A^1$ , and  $q_B(R) = \bar{q}_B(R)/M_B^1$ . This representation of these isotopomer-independent correction functions has been incorporated into a general program for performing direct potential fits to spectroscopic data, which will be available for distribution in the near future.<sup>2</sup>

Use of this improved representation resolves all of the prob-

<sup>2</sup> Program “DSPotFit” (Diatomic Singlet Potential Fits), by J. Y. Seto and R. J. Le Roy, will be available on request from leroy@UWaterloo.ca in the near future.

lems identified above. In particular, for problem number 1, the adiabatic potential correction functions now have units simply in  $\text{cm}^{-1}$ , and the centrifugal potential correction functions are dimensionless; for number 4, except for D or T isotopes in hydrides, the mass ratios in Eq. [17] are always close to unity, so the strengths of the  $q_A(R)$  and  $q_B(R)$  functions are direct indications of their importance; for number 7, the effective adiabatic potential for the dominant isotopomer  $V_{ad}^1(R)$  will not change significantly when data for minority isotopomers are added to the fit; for number 8, the fitted  $V_{ad}^1(R)$  function is the real effective potential for an actual molecular system, and its uncertainties beyond the range of the minority isotopomer data will not be affected by the extrapolation uncertainties in the adiabatic potential correction functions; and for number 9, the use of a dominant isotopomer as the reference system facilitates fitting to determine to field-shift corrections (18).

## VI. DISCUSSION AND CONCLUSIONS

This paper presents and tests new means of representing atomic mass-dependent JWKB and Born–Oppenheimer breakdown corrections in parameter or potential energy function representations of diatom level energies, which resolve a variety of problems associated with conventional representations. As in the conventional approach, the resulting expansion coefficients or correction functions are isotopomer independent, although they are defined assuming a particular choice of reference isotopomer. These formulations have been incorporated into general fitting programs for simultaneously treating various types of multi-isotopomer data for one or several electronic states, which are or will be available on request from the author. Application of the parameter-fitting program to selected infrared and microwave data for HF and DF has yielded the current best Dunham-type expansion parameters for the lower vibrational levels of that system.

Some spectral analyses place great emphasis on the determination of a “true”  $R_e$  value and focus on the use of the  $U_{0,1}$  value from Eq. [4] to determine it. The recommended change of representation has no effect on such discussions, since Eq. [7] shows that  $U_{0,1}$  may readily be generated from the fitted  $Y_{0,1}^1$ ,  $\delta_{l,m}^A$ , and  $\delta_{l,m}^B$  values. The general emphasis of the present approach is to fit data to a model in which the parameters determined represent, insofar as possible, the properties of real molecules, rather than the features of some underlying theoretical model. At the same time, since the recommended representations of Eqs. [5], [11], and [16] incorporate all of the appropriate functional behavior, their interpretation in terms of conventional theoretical models (using, e.g., Eqs. [6] and [7]) may be readily undertaken in subsequent analysis.

One apparent deficiency of the empirical parameter-fitting approach is that band constants for  $m \geq 2$  determined from empirical fits to Eqs. [5] and [11] may not be exactly mechanically consistent with the lower order ones, in that they may not

be the correct quantal centrifugal distortion constants implied by the (adiabatically adjusted) potential defined by the ( $m = 0$  and 1)  $G(v)$  and  $B_v$  expansions. This almost inevitably occurs for the highest order (largest  $m$ ) distortion constants considered, as the physical significance of the highest order coefficients determined in any power series expansion fit tends to be lost. Although this has no effect on the ability of the fitted parameters to represent accurately the input data, they will be increasingly unreliable in extrapolations to higher  $J$ . Fortunately, a solution to this problem is readily obtained by using the fitted  $m = 0$  and 1 parameters to generate a potential by the RKR inversion procedure (35–39), numerically calculating all required centrifugal distortion constants using standard methods (40–42), and holding the latter fixed in a subsequent fit to Eq. [5] or [11] to determine improved and mechanically consistent  $G(v)$  and  $B_v$  expansions. This iterative approach converges rapidly and has been successfully used in several practical applications (43–45, 14, 15). An alternate algebraic method to constrain the higher order ( $m \geq 2$ ) parameters to be consistent with those of lower order, while taking account of Born–Oppenheimer breakdown effects, has been developed by Ogilvie and co-workers (46–50).

Finally, it is important to note that this paper is not the first to propose or introduce the use of a real physical isotopomer as the reference relative to which Born–Oppenheimer breakdown corrections are defined. In particular, Tiemann (11) used the mass shift  $\Delta M_A^\alpha/M_A^\alpha$  for scaling the mass-dependent isotopomer corrections both to the  $Y_{0,1}$  rotational constants and to the spin–rotation and spin–spin coupling parameters for ground state SO, an approach adopted in subsequent work in both his (16–18) and other (51, 52) groups. However, the present work does appear to be the first occasion on which a recommendation to use this approach in general to supplant Eq. [4] has been presented and justified.

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