dParFit: A computer program for fitting diatomic molecule spectral data to parameterized level energy expressions

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A B S T R A C T

This paper describes FORTRAN program **dParFit**, which performs least-squares fits of diatomic molecule spectroscopic data involving one or more electronic states and one or more isotopologues, to parameterized expressions for the level energies. The data may consist of any combination of microwave, infrared or electronic vibrotational bands, fluorescence series or binding energies (from photo-association spectroscopy). The level energies for each electronic state may be described by one of: (i) band constants $\{G_v, B_v, D_v, \ldots\}$ for each vibrational level, (ii) generalized Dunham expansions, (iii) pure near-dissociation expansions (NDEs), (iv) mixed Dunham/NDE expressions, or (v) individual term values for each distinct level of each isotopologue. Different representations may be used for different electronic states and/or for different types of constants in a given fit (e.g., G_v and B_v may be represented one way and centrifugal distortion constants another). The effect of Λ-doubling or $^2\Sigma$ splittings may be represented either by band constants (q_v^B or γ_v^B, q_v^D or γ_v^D, etc.) for each vibrational level of each isotopologue, or by using power series expansions in $(v+\frac{1}{2})$ to represent those constants. Fits to Dunham or NDE expressions automatically incorporate normal first-order semiclassical mass scaling to allow combined analyses of multi-isotopologue data. In addition, **dParFit** may fit to determine atomic-mass-dependent terms required to account for breakdown of the Born–Oppenheimer and first-order semiclassical approximations. In any of these types of fits, one or more subsets of these parameters for one or more of the electronic states may be held fixed, while a limited parameter set is varied. The program can also use a set of read-in constants to make predictions and calculate deviations [$y_{calc} - y_{obs}$] for any chosen input data set, or to generate predictions of arbitrary data sets.

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1. Introduction

In recent decades, the increasing sophistication, accuracy and productivity of experimental methods has led to an explosion in the extent and accuracy of the spectroscopic data sets being reported for molecular systems. However, in spite of ubiquitous access to powerful computers, much data analysis has still tended to focus on individual isolated data sets, rather than being comprehensive. The program described herein was developed to address the need for a flexible, robust tool for performing least-squares fits of large and/or diverse data sets for diatomic molecules in singlet or $^2\Sigma$ electronic states, to parameterized expressions for the molecular level energies. It can simultaneously fit to any combination of microwave (pure rotational), and/or infrared (vib-rotational) and/or electronic vibrotational bands, fluorescence series, or photoassociation spectroscopy binding energies, involving one or more singlet or $^2\Sigma$ electronic states and one or more isotopologues. The

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levels for each electronic state may be represented in a variety of ways that are described below, and Λ-doubling or $^2\Sigma$ splitting is treated explicitly. The code allows data for multiple isotopologues of a single molecular system to be treated simultaneously in combined-isotopologue analyses in order both to obtain compact unified energy level descriptions, and to allow the determination of atomic-mass-dependent Born–Oppenheimer and first-order semiclassical breakdown correction terms.

In the following, Section 2 describes the level energy expressions that may be fitted to, and outlines some of the program's options. Section 3 then states the input/output conventions, indicates the units assumed for the various parameters, and describes a convenient way of running the program on a UNIX or Linux system. The program's operation is controlled by the contents of two data files: the first contains the experimental data, while the second contains parameters that identify the nature of the system and specify the type of fit to be performed. The structure of these data files and the significance of the various read-in control parameters are described in Appendices A and B, respectively, in the Supplementary Material file, while Appendix C there presents and describes input and output files for three illustrative cases. Appendix D then presents an outline of the structure of the program and the roles of its various subroutines. The extensively commented Fortran source code for the current version of **dParFit** (an acronym for **d**iatomic **Par**ameter **Fit**ting) is available as part of the Supplementary Material on the Journal's www site, together with illustrative plain-text "instruction" data files for the cases described in Appendix C. Any changes from the (unpublished) most recent previous versions of this code [1] are cosmetic in nature. The author would appreciate having users inform him of any apparent errors or instabilities in the code, and of additional features which might appear desirable for future versions.

2. Theoretical background, expressions used, and program options

2.1. General considerations, and treatment of multiple isotopologues

The parameters representing the level energies for each electronic state are divided into five groups, for most of which one can make a variety of choices for the type of representation to be used. The first group consists of the vibrational energies $\{G_v\}$, the second the inertial rotational constants $\{B_v\}$, and the third the centrifugal distortion constants $\{D_v, H_v, \ldots\}$. The fourth group is then the set of parameters characterizing Λ-doubling constants for singlet electronic states with $\Lambda > 0$, or for Hund's case-c coupling [2], with $\Omega \neq 0$, or for the analogous constants characterizing spin-rotation splitting in $^2\Sigma$ states. Finally, the fifth group is the set of parameters defining atomic-mass-dependent terms characterizing breakdown of the Born–Oppenheimer approximation and of the first-order semiclassical (or JWKB) approximation, which are grouped together and collectively called "BOB" corrections, since

the type of parameter-fitting used herein cannot distinguish between them.

In the expressions for these quantities given below, the label "α" is used to identify a particular isotopologue of the system. The fact that **dParFit** is designed for (but not restricted to) treating multi-isotopologue data sets means that most parameter symbols include the subscript or superscript label "α". While this introduces some clutter to the notation, it cannot be avoided. However, it is important to realize that except for band-constant or term-value fits, in which independent parameter values are determined for each vibrational (or vibration–rotation) level of each isotopologue, the only free parameters for each electronic state are those for the reference isotopologue, which is labelled $\alpha = 1$; values for all other isotopologues are determined from the isotopologue-1 values using normal semiclassical mass scaling and (when appropriate) addition of atomic-mass-dependent BOB corrections (see Section 2.6). As discussed in Ref. [3], this reference isotopologue would normally be chosen to be the most abundant isotopologue, since intensity considerations mean that the most extensive data sets are usually available for that species. However, a user may make whatever choice they wish.

The current version of **dParFit** can treat transitions of $^2\Sigma$ electronic states or of *singlet* states (or states which may be effectively treated as singlets) associated with any value of the electronic orbital angular momentum projection quantum number Λ. For $\Lambda > 0$, the centrifugal variable appearing in the Hamiltonian and in expressions for the "mechanical" J-dependence of the level energies is $[J(J+1) - \Lambda^2]$, while that associated with Λ-doubling splittings is $[J(J+1)]^\Lambda$. While the latter is technically only correct for $^1\Pi$ splittings [4], its use to represent perturbations for $^1\Delta$ or $^1\Phi$ states will introduce little error. As usual, for Hund's case-c non-singlet states with $\Omega \neq \Lambda$ (such as the $A^3\Pi(1_u)$ state of I_2), this means that in the expressions presented below the symbol Λ actually represents the value of Ω. Note, however, that the current version of **dParFit** only allows for *integer* case-c values of Ω.

2.2. Representations for G_v and for B_v

The first four methods of representing level energies described here all assume an explicit partitioning into a distinct vibrational energy plus a separate terms representing each order of dependence on the rotational quantum numbers. A fifth approach, in which individual term values are used for each distinct level, is discussed in Section 2.7. **dParFit** allows a user to choose among four possible ways of representing the vibrational energies $\{G_v\}$, and the inertial rotational constants $\{B_v\}$.

2.2.1. Band constant expressions

The first type of level-energy representation involves the use of a set of "band constants" $\left\{ K_m^{(\alpha)}(v) \right\} = \left\{ G_v^{(\alpha)}, B_v^{(\alpha)}, -D_v^{(\alpha)}, H_v^{(\alpha)}, \ldots \right\}$ for each vibrational level of each isotopologue, α:

$$E^{(\alpha)}(v,J) = \sum_{m=0}^{} K_m^{(\alpha)}(v) \left[J(J+1) - \Lambda^2 \right]^m$$

$$= G_v^{(\alpha)} + B_v^{(\alpha)} \left[J(J+1) - \Lambda^2 \right] - D_v^{(\alpha)} \left[J(J+1) - \Lambda^2 \right]^2$$
$$+ H_v^{(\alpha)} \left[J(J+1) - \Lambda^2 \right]^3 + \cdots \tag{1}$$

in which independent values of each parameter $K_m^{(\alpha)}(v)$ must be determined for each vibrational level of each isotopologue, α. Note that $K_2^{(\alpha)}(v) = -D_v^{(\alpha)}$ is the quadratic coefficient actually reported by the program.

This band-constant mode effectively allows for traditional band-by-band fits, with the improvement that all bands associated with a given vibrational level of a given isotopologue would be constrained to yield a single set of consistent band constants. To take account of cases in which J-dependent perturbations make the rotational constants vary irregularly from one level to the next while the vibrational energies are unaffected, the code also allows G_v to be represented by Dunham, NDE or MXS expansions (see below) while the rotational constants (B_v and/or centrifugal distortion constants) are represented by band constants. However, if the G_v values are to be represented by band constants, the same *must* be true for all of the rotational constants. Similarly, if B_v values are treated as band constants (when the G_v values are not), the same must be true for the CDC's.

2.2.2. Dunham expansions

The second type of representation defines G_v and B_v as the $m = 0$ and 1 components of the conventional Dunham term-value expression [2,5,6]

$$E^{(\alpha)}(v, J) = \sum_{m=0} \sum_{l=0}{}' Y_{l,m}^{(\alpha)} (v+1/2)^l \left[J(J+1) - \Lambda^2 \right]^m$$
$$= \sum_{m=0} \sum_{l=0}{}' Y_{l,m}^{(1)} (\mu_1/\mu_\alpha)^{m+l/2} (v+1/2)^l \left[J(J+1) - \Lambda^2 \right]^m \tag{2}$$

in which the prime (') on the sum over l denotes the fact that for $m = 0$ the summation actually starts at $l = 1$, and μ_α is the conventional two-body reduced mass of isotopologue-α (see Section 3). The final version of this expression incorporates the familiar first-order semiclassical mass-scaling relation for parameters associated with different isotopologues:

$$Y_{l,m}^{(\alpha)} = (\mu_1/\mu_\alpha)^{m+l/2} Y_{l,m}^{(1)} \tag{3}$$

as well as the associated assumption that $Y_{0,0}^{(\alpha)} \equiv 0$ [5]. Corrections to these approximations are discussed in Section 2.6. For G_v and B_v the resulting Dunham expansions are therefore

$$G_v^{(\alpha)} = K_0^{(\alpha)}(v) = \sum_{l=1} Y_{l,0}^{(\alpha)} (v+1/2)^l$$
$$= \sum_{l=1} Y_{l,0}^{(1)} (\mu_1/\mu_\alpha)^{l/2} (v+1/2)^l \tag{4}$$

$$B_v^{(\alpha)} = K_1^{(\alpha)}(v) = \sum_{l=0} Y_{l,1}^{(\alpha)} (v+1/2)^l$$
$$= \sum_{l=0} Y_{l,1}^{(1)} (\mu_1/\mu_\alpha)^{1+l/2} (v+1/2)^l \tag{5}$$

Thus, independent of the number of isotopologues considered simultaneously, the only "free" parameters are the $\{Y_{l,m}^{(1)}\}$ values for the selected reference isotopologue, $\alpha = 1$.

2.2.3. Near-dissociation expansions for G_v and B_v

The third type of functional representation allowed by **dParFit** is pure "near-dissociation expansions" (NDEs), which incorporate the theoretically known limiting near-dissociation behaviour of the given quantity [7–10] into an expression that includes empirical parameters to be determined from the experimental data [11–14]. Just as conventional Dunham expressions are expansions about the limiting case of harmonic-oscillator/rigid-rotor behaviour at the potential minimum, NDE functions are expansions about the theoretically known limiting functional behaviour at dissociation [7–10], and hence they are much more reliable for extrapolating to high v beyond the range of observed data [12,13,15], and for providing compact representations of data sets that span a large fraction of the potential well [11,14,16]. The rest of this sub-subsection describes the use of NDE expressions and their parameterization in program **dParFit**; interested readers may wish to review associated theory and review papers [7–10,13,17–20] and illustrative applications of this approach [12,14,16,21–23].

The theory underlying NDE expressions for vibrational energies, rotational constants, and other properties of vibrational levels lying near dissociation is based on the fact that properties of such levels depend mainly on the shape of the potential energy function near their outer turning points [8]. As a result, their v-dependence is mainly determined by the limiting asymptotic behaviour of the intermolecular potential, which in all cases has the simple inverse power form

$$V(r) = \mathfrak{D} - C_n/r^n \tag{6}$$

in which $\mathfrak{D}$ is the energy at the dissociation limit, the power n is determined by the nature of electronic states of the atoms formed when the given molecular state dissociates (and is generally known) [8,17], and reliable estimates of the limiting long-range coefficient C_n are often available from theory. Of course, near-dissociation theory and NDE expression are only applicable to bound electronic states for which this C_n coefficient is positive (attractive). **dParFit** assumes that both n and C_n are known, and holds them fixed at read-in values provided by the user.

The NDE representation for the vibrational energies of isotopologue-α may be written as

$$G_v^{(\alpha)} = K_0^{(\alpha)}(v) = \mathfrak{D} - K_0^{(\alpha),\infty}(v) \times \mathcal{F}_0^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v) \tag{7}$$

and those for the inertial rotation ($B_v^{(\alpha)} = K_1^{(\alpha)}(v)$) and centrifugal distortion ($K_m^{(\alpha)}(v)$ for $m \geq 2$) constants as

$$K_m^{(\alpha)}(v) = (\mu_1/\mu_\alpha)^m K_m^{\{\alpha\},\infty}(v) \times \mathcal{F}_m^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v) \tag{8}$$

in which $v_{\mathfrak{D}}^{(\alpha)}$ is the (non-integer) effective vibrational index of isotopologue-α at dissociation [8], $\mathcal{F}_m^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v)$ are empirical expressions that are required to approach unity as v approaches $v_{\mathfrak{D}}^{(\alpha)}$, and the theoretically known limiting near-dissociation behaviour of the vibrational binding energy and rotational constants is given by the

expressions [7–9,18],

$$K_m^{(\alpha),\infty}(v) = (\mu_1/\mu_\alpha)^{[n/(n-2)]-m} X_m^{(1)}(n, C_n) \left(v_{\mathfrak{D}}^{(\alpha)} - v\right)^{[2n/(n-2)]-2m}$$

(9)

in which $X_m^{(1)}(n, C_n) = \overline{X}_m(n)/[(\mu_1)^n (C_n)^2]^{1/(n-2)}$ and $\overline{X}_m(n)$ is a known numerical factor depending only on the physical constants and the value of the integer n [8,9,18]. Normal first-order semiclassical mass scaling [5,24] shows that the values of $v_{\mathfrak{D}}^{(\alpha)}$ for different isotopologues are interrelated *via* the expression

$$(v_{\mathfrak{D}}^{(\alpha)} + 1/2) = \sqrt{\mu_1/\mu_\alpha} \left(v_{\mathfrak{D}}^{(1)} + 1/2\right).$$

(10)

While this equation is not precisely correct, the current version of **dParFit** is not able to allow for corrections to it.

The free parameters in this NDE representation are therefore the physically significant quantities $\mathfrak{D}$ and $v_{\mathfrak{D}}^{(1)}$, and the empirical parameters defining the $\mathcal{F}_m^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v)$ functions. Note that the quantity $v_{\mathfrak{D}}^{(\alpha)}$ appearing in these expressions has the same value for all rotational orders m.

As in most published work using NDE functions, **dParFit** allows the empirical function $\mathcal{F}_m^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v)$ for G_v or B_v to be represented as a rational polynomial or power of a rational polynomial [15,16,18,21,23]

$$\mathcal{F}_m^{(\alpha)}\left(v_{\mathfrak{D}}^{(\alpha)} - v\right) = \left(\frac{1 + \sum_{i=t}^{L} p_i^{(\alpha),m} \left(v_{\mathfrak{D}}^{(\alpha)} - v\right)^i}{1 + \sum_{j=t}^{M} q_j^{(\alpha),m} \left(v_{\mathfrak{D}}^{(\alpha)} - v\right)^j}\right)^{\mathcal{S}},$$

(11)

in which the exponent power $\mathcal{S}$ is set at either $\mathcal{S} = 1$, to yield what is called an "outer" expansion, or $\mathcal{S} = \frac{2n}{n-2}$, for G_v and $\mathcal{S} = \frac{2n}{n-2} - 2$ for B_v, to yield an "inner" expansion. An alternate form of $\mathcal{F}_m^{(\alpha)}$ which *may* be used for $G_v^{(\alpha)}$ or $B_v^{(\alpha)}$, and is the *only* NDE form allowed by **dParFit** for centrifugal distortion constants ($K_m^{(\alpha)}(v)$ for $m \geq 2$), is [14,16,21]

$$\mathcal{F}_m^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v) = \exp\left\{\sum_{i=t} p_i^{(\alpha),m}\left(v_{\mathfrak{D}}^{(\alpha)} - v\right)^i\right\}.$$

(12)

In both of Eqs. (11) and (12) the expansion parameters for different isotopologues α are related by the usual first-order semiclassical mass-scaling relationship: $p_i^{(\alpha),m} = (\mu_1/\mu_\alpha)^{1/2} \; p_i^{(1),m}$ and $q_j^{(\alpha),m} = (\mu_1/\mu_\alpha)^{1/2} q_j^{(1),m}$, and the numbers $(L+1-t)$ or $(M+1-t)$ of unique empirical numerator and/or denominator coefficients $p_i^{(1),m}$ and $q_i^{(1),m}$, respectively, depend on the nature and extent of the data. Moreover, for some cases, the most appropriate value of the leading expansion order t is known from theory. In particular, if the leading terms in the attractive long-range potential $V(R) \simeq \mathfrak{D} - \sum_{m=n} C_m/R^m$ have powers $m = 6$ and 8, $t = 1$ for the vibrational ($m = 0$) expansion; if they are $m = 4$ and 6, then $t = 2$; and if they are $m = 3$ and 6, $t = 4$; while if the leading powers differ by 1, (e.g., $m = 5$ & 6 or $m = 4$ & 5), the leading correction is precisely zero, and one should set $t \geq 2$ [15,19].

Although some properties of NDEs are prescribed by theory (e.g., the values of n and C_n, and for some cases, also of t), there is in general no *a priori* means of selecting the optimal form of this expansion to be used for a given case (i.e., for making a particular choice of the power $\mathcal{S}$ and of the numbers of numerator $(L+1-t)$ and denominator $(M+1-t)$ expansion terms) [11,12,14,15]. However, use of

a (relatively) simple companion program **GvNDE** that automatically fits a given set of vibrational energies to all forms of Eqs. (11) and (12) consistent with a given total number of expansion parameters and selected t value [25] will allow a user both to select a preferred form for a given case (i.e., preferred values of $\mathcal{S}$, L, M and t), and to provide the realistic initial trial values of the $\{p_i^{(1),m}\}$ and/or $\{q_j^{(1),m}\}$ parameters required to initiate the non-linear least-squares fitting procedure.

While they are somewhat more complicated to use, NDE expressions have some significant advantages over conventional Dunham expansions.

- Because they explicitly incorporate the theoretically-known limiting near-dissociation behaviour of vibrational energies and other properties, they are much more reliable for extrapolating to estimate the dissociation energy and the number, energies and properties of unobserved vibrational levels. In contrast, as with all polynomial functions, Dunham expansions are notoriously unreliable for performing extrapolations.
- For systems in which the experimental data span a large fraction of the potential well, NDE functions tend to be more compact than Dunham expansions which yield fits of equivalent quality, since the dense manifold of levels near dissociation is represented by a relatively modest number of empirical expansion parameters.

In any case, if one wishes to use NDE functions to represent the vibrational energies or rotational constants of a given electronic state, it is necessary: (i) to determine in advance (from theory) the values of n and C_n, and when possible (see above) also of t, appropriate to the particular molecular state [8,17,19], (ii) to select the values of $\mathcal{S}$, L and M to define the chosen form of $\mathcal{F}_m^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v)$, and (iii) to provide realistic initial trial values of $\mathfrak{D}$, of $v_{\mathfrak{D}}^{(1)} = v_{\mathfrak{D}}^{(\alpha=1)}$, and of the expansion parameters $\{p_i^{(1),m}\}$ and $\{q_j^{(1),m}\}$. As mentioned above, the latter may be obtained from preliminary application of the companion program **GvNDE** to preliminary sets of vibrational energies or B_v values [25]. Note that, as with fits to Dunham expansions, performing a multi-isotopologue fit to NDE functions is just as straightforward as fitting to data for a single isotopologue, with the fit determining parameter values specific to the reference isotopologue ($\alpha = 1$) while values for other isotopologues (calculated and printed by **dParFit**) are determined by the first-order semiclassical mass-scaling relation, and BOB terms are included, as appropriate (see Section 2.6).

One final point unique to the use of NDE expressions concerns the determination of the dissociation limit $\mathfrak{D}$. One of the main advantages of NDE-type representations is the fact that they provide optimal predictions of the distance from the highest observed vibrational levels to $\mathfrak{D}$ (if $\mathfrak{D}$ is allowed to vary in the fit), and of the number, energies and other properties of unobserved high-lying vibrational levels. However, the absolute values of $\mathfrak{D}$ for different electronic states differ by the known atomic energy level spacings of the atoms formed when those molecular states dissociate. Thus, in any analysis involving multiple electronic states, only one value of $\mathfrak{D}$ is truly independent, and all others are determined by the

combination of that value with the known atomic level spacings. As a result, in **dParFit**, the value of $\mathfrak{D}$ ($\equiv$ DLIMIT in the input data file) for the first electronic state treated using an NDE (or MXS, see below) expression for G_v is treated as the free or dissociation-limit-defining parameter, while those for other NDE-represented states are fixed relative to the first using the differences between the read-in values of DLIMIT.

2.2.4. "MXS" mixed near-dissociation/Dunham expansions for G_v and B_v

When pure Dunham expansions or pure NDE functions are used to represent a large number of vibrational levels spanning a large fraction of a potential energy well, difficulties are sometimes encountered. In particular, realistic trial parameters for very high-order pure NDE functions are difficult to generate, and for either type of representation, fits tend to become unstable for sufficiently high-order expansions. The latter problem could probably be addressed by using quadruple-precision (REAL ∗ 16) arithmetic in the least-squares procedure, but introducing this capability into the code would tend to make it less portable and more difficult to use, and uncertainties regarding finite precision numerical rounding could make the resulting parameter sets inconvenient to use.

Tellinghuisen has shown that these problems can be resolved by using mixed representations consisting of a Dunham-type power series for levels lying in the lower part of the potential energy well and an NDE expansion for levels lying near dissociation [26,27]. This type of expression is also expected to prove useful for describing the properties of "shelf" states, for which there is an abrupt change in the character of the v-dependence of G_v and B_v at the onset of the shelf. **dParFit** offers the option of fitting to G_v or B_v using the "MXS" mixed-representation function introduced by Tellinghuisen [27]. For some chosen switch-over point $v = v_s$, this form uses

- a normal Dunham polynomial (see Section 2.2.2) for $v \lesssim v_s$ and
- a near dissociation expansion (see Section 2.2.3) for $v \gtrsim v_s$,

and merges the two at that chosen $v = v_s$ using the switching function,

$$F_s(v) = \left\{ 1 + \exp\left(\frac{v - v_s}{\delta v_s}\right) \right\}^{-1} \tag{13}$$

to yield the MXS expressions

$$G_v^{\text{MXS}} = F_s(v)G_v^{\text{Dun}} + [1 - F_s(v)]G_v^{\text{NDE}} \tag{14}$$

$$B_v^{\text{MXS}} = F_s(v)B_v^{\text{Dun}} + [1 - F_s(v)]B_v^{\text{NDE}} \tag{15}$$

In a fit using MXS functions for G_v or B_v, it is necessary to specify the order of the Dunham polynomial to be used, and to specify the particular NDE form and initial trial values of the physically significant variables $\mathfrak{D}$ and $v_{\mathfrak{D}}$, and of the various expansion parameters defining the NDE function, as well as values for the (normally fixed) parameters v_s and δv_s defining the switching function. As mentioned above, initial trial values of required NDE

parameters may be obtained by fitting preliminary estimates of G_v (or B_v) for $v \geq v_s$ to pure NDE functions using a program such as **GvNDE** [25]. For "regular" (i.e., non-shelf) states, the method has been found to be fairly insensitive to the particular choice of v_s or δv_s. However, problems can occur if δv_s is too large, and a default value of $\delta v_s = 1$ appears to be adequate for most cases. The value of v_s should be one which requires the use of only a modest number of NDE function parameters: current experience suggests that a good choice would be $v_s \approx v_{\mathfrak{D}}/2$, although other choices would probably serve equally well [28]. In order to allow v_s and δv_s to be treated as free parameters in fits to data involving shelf states, **dParFit** reads and represents both v_s and δv_s as floating-point variables. However, unless one is trying to perform fits to data for a shelf state, both v_s and δv_s normally should be fixed at integer values and not varied in the fit.

Note that the type of representation used for B_v (i.e., band constants *vs.* Dunham *vs.* pure NDE *vs.* MXS) need not be the same as that used for G_v. However, **dParFit** does not allow the B_v representation to be "more sophisticated" than that for G_v. In particular, if G_v is represented by band constants, the same must be true for B_v and the centrifugal distortion constants; if G_v is represented by a Dunham expansion, the rotational constants may be represented by band constants or Dunham expansions, but not by NDE or MXS functions; if G_v is represented by a pure NDE function, B_v may be represented by band constants or by a Dunham or pure NDE function, while if G_v is represented by an MXS function, B_v may be represented using any of the four representations.

2.3. Representations for centrifugal distortion constants (CDCs)

2.3.1. There are three choices regarding how to represent the CDCs

dParFit gives a user three choices for how to represent the centrifugal distortion constants (CDCs), $\{K_m^{(\alpha)}(v)\}$ of Eq. (1) with $m \geq 2$. The first is simply as band constants, with an independent value of $K_m^{(\alpha)}(v)$ being determined (or specified) for each vibrational level of each isotopologue. This choice is invoked automatically if either G_v's or B_v's are treated as band constants. If CDC's are to be fitted as band constants, then any Λ-doubling or $^2\Sigma$-splitting contributions must also be fitted as band constants.

The second choice is to use Dunham expansions, with each distortion constant being represented as

$$K_m^{(\alpha)}(v) = \sum_{l=0} Y_{l,m}^{(\alpha)} (v + 1/2)^l = \sum_{l=0} Y_{l,m}^{(1)} (\mu_1/\mu_\alpha)^{m+l/2} (v + 1/2)^l. \tag{16}$$

As for G_v and B_v, in a combined-isotopologue analysis the only free parameters are those for isotopologue-1, $\{Y_{l,m}^{(1)}\}$, with those for other isotopologues being determined by mass-scaling relation of Eq. (3).

The third choice of representation for CDCs is the exponential pure NDE form of Eqs. (8), (9) and (12). However, **dParFit** places two limitations on this choice. The first is that it may only be used if G_v is represented by

an NDE or MXS function. This is necessary since the value of $v_{\mathfrak{D}}^{(\alpha)}$ is defined by the behaviour of the vibrational energies, and the same values of n, C_n and $v_{\mathfrak{D}}$ are shared by the NDE expressions for all properties. The second limitation is that centrifugal distortion constants may only be represented by NDE expressions if they are to be held fixed in the fit. It is well known that CDC constants obtained from empirical fits are generally "effective" distortion parameters which often have substantially incorrect magnitudes and sometimes also incorrect sign, particularly for the higher-order (larger m) CDC s (see, e.g., Fig. 5 of Ref. [16]), even if they do provide an accurate representation of the available data. As a result, requiring such empirical functions to have the correct limiting near-dissociation behaviour would seem quite pointless, and might give rise to spurious oscillations or instabilities.

2.3.2. Fits with fixed "mechanically consistent" CDCs

It is now fairly common to use preliminary G_v and B_v functions to generate an RKR potential energy curve [29,30] which in turn is used in a quantal calculation [31–33] to compute "true" values of the CDC constants implied by that potential energy function. Holding the CDC s fixed at those calculated values while performing a new fit to the data should then yield improved G_v and B_v functions, which in turn yield an improved RKR potential, from which one can generate further improved CDC values. This iterative procedure generally converges quite rapidly [14,34,35]. The resulting vibrational and rotational constants are referred to as being "mechanically consistent", in that within the accuracy of the first-order JWKB approximation on which the RKR procedure is based, they are precisely consistent with the "mechanical" description of the molecule provided by that potential energy curve. Moreover, physically meaningful values of high-order CDCs are much more readily obtained by this procedure than from empirical fits, so results obtained in this way are usually much more reliable for extrapolation to J values beyond the range spanned by the experimental data.

To facilitate such iterative analyses, **dParFit** has the ability to read and hold fixed values of CDC constants defined by read-in parameters. They may be input using any of band-constant, Dunham or pure-NDE function formats. This is the only context in which NDE functions to represent the CDC s are allowed by **dParFit**. At the same time, since CDC constants of increasing rotational order are known to have increasingly high-order singularities at dissociation [10,13,18], NDE functions are in fact the *only* meaningful way of representing them analytically for levels approaching dissociation [13,14,16]. Note, however, that the only NDE expression for CDCs that is allowed by **dParFit** is the exponential function of Eq. (12), which has the limitation that it cannot change sign. This is appropriate for levels lying near dissociation, for which region theory tells us that to all orders the CDCs make negative contributions to the rotational energy [10,13,18], and it is also appropriate for *all* levels of some molecular states [14,16]. However, it is not true for all states, especially at low v. On the other hand, numerically calculated CDC values may readily be introduced and held fixed using the "band-constant" option, so this limitation of the utility of NDE expressions for CDC

constants in no way limits use of the iterative self-consistent treatment of CDCs in practical data analyses.

A cautionary practical note. The most widely used publicly available program for calculating CDCs from a known potential function will only generate the first six, from D_v to O_v [33,36] In extreme cases, these six constants may not suffice to represent centrifugal distortion effects to full experimental accuracy for very high-J data. If this occurs, the only solution with the present code would be to use input parameter JTRUNC to limit the range of rotational data considered in the analysis.

2.4. Treatment of spin-singlet $\Lambda > 0$ states: representations for Lambda doubling

For spin-singlet states with electronic angular momentum projection quantum number $\Lambda > 0$, the "mechanical" contribution to the rotational energy depends on powers of $[J(J+1)-\Lambda^2]$ rather than of $[J(J+1)]$ [37]. Moreover, every rotational level is split into a doublet of e and f rotational parity states, with a splitting that is proportional to $[J(J+1)]$, and the band-constant type coefficient defining its magnitude varies with isotopologue, with vibrational energy, and with the degree of (mechanical) centrifugal distortion [2,4]. **dParFit** represents such splittings by an additive energy correction expressed using either a band-constant or a Dunham-expansion type of representation:

$$\delta E_\Lambda^{(\alpha)}(v, J, \{e/f\}) = \mathrm{sg}(\{e/f\})\,[J(J+1)]^\Lambda$$
$$\sum_{m=\Lambda} q_m^{(\alpha)}(v)\left[J(J+1)-\Lambda^2\right]^{m-\Lambda} \tag{17}$$

$$= \mathrm{sg}(\{e/f\})[J(J+1)]^\Lambda \sum_{m=\Lambda}\sum_{l=0} q_{l,m}^{(\alpha)}(v+1/2)^l\left[J(J+1)-\Lambda^2\right]^{m-\Lambda}$$

$$= \mathrm{sg}(\{e/f\})[J(J+1)]^\Lambda \sum_{m=\Lambda}\sum_{l=0} q_{l,m}^{(1)}\left(\frac{\mu_1}{\mu_\alpha}\right)^{\Lambda+m+\frac{l}{2}}$$
$$(v+1/2)^l\left[J(J+1)-\Lambda^2\right]^{m-\Lambda}. \tag{18}$$

Here, $\mathrm{sg}(\{e/f\})$ is a factor whose value depends on whether the level in question has e or f parity, and is defined such that such that $[\mathrm{sg}(e)-\mathrm{sg}(f)]=1$. In common empirical treatments these factors are usually defined as $\mathrm{sg}(e)=+1/2$ and $\mathrm{sg}(f)=-1/2$. However, **dParFit** allows a user to make other choices for them.

As discussed in Refs. [4,38,39], the level splitting for a diatomic molecule in a singlet electronic state occurs because of non-adiabatic coupling of the e and/or f sublevels for a given J to levels with the same rotational parity in a nearby perturbing $^1\Sigma^+$ or $^1\Sigma^-$ state. If that perturbing state has $^1\Sigma^+$ symmetry, all its levels have e parity, so it can only perturb e parity levels of the other state; conversely, if the perturbing state has $^1\Sigma^-$ symmetry, it will only perturb the f sublevels. Thus, if the dominant Λ-doubling perturbations affecting the levels of a given $\Lambda > 0$ state are due to a nearby $^1\Sigma^+$ state, then its f sublevels will be unaffected and only the e sublevels will be shifted. In this case it would be most appropriate to define $\mathrm{sg}(e)=+1$ and $\mathrm{sg}(f)=0$. Similarly, if the dominant perturbing state

has $^1\Sigma^-$ symmetry, one should set $\text{sg}(e) = 0$ and $\text{sg}(f) = -1$. For each $\Lambda > 0$ state considered in an analysis, **dParFit** requires a user to select one of these options. Note that the exponent power Λ and the lower bound on the first summation in Eqs. (17) and (18) reflect the fact that for Π states ($\Lambda = 1$) the splitting arises in second-order perturbation theory, for Δ states ($\Lambda = 2$) in fourth-order perturbation theory, for Φ states ($\Lambda = 3$) in sixth-order perturbation theory, etc. [38].

As shown by Eq. (18), the isotopologue mass-dependence of Λ-doubling splitting constants

$$q_{l,m}^{(\alpha)} = (\mu_1/\mu_\alpha)^{\Lambda+m+l/2} q_{l,m}^{(1)}, \tag{19}$$

differs from that for the conventional rotational constants (see Eq. (3)) by an additional factor of $(\mu_1/\mu_\alpha)^\Lambda$. Moreover, while normal rotational and centrifugal distortion constants depend on the properties of the potential energy function and moments of the $1/r^2$ centrifugal radial function, the magnitudes of Λ-doubling splittings depend on moments of a function with a qualitatively different radial behaviour [39]. This suggests that if Λ-doubling affects only (say) the e-parity sub-levels, and not the f-parity sublevels, the quality of fit would be distinctly better if one used $\text{sg}(e) = +1$ and $\text{sg}(f) = 0$ in Eq. (18), rather than one of the two other choices. While such differences are expected to be fairly small, they should sometimes be observable. If such differences is observable, it would mean that the fit is able to identify the symmetry of the dominant perturbing state ($^1\Sigma^+$ *vs.* $^1\Sigma^-$) responsible for the splitting [39]. In any case, **dParFit** allows a user to study such questions by requiring the user to select a particular $\text{sg}(\{e/f\})$ convention when fitting to determine Λ-doubling splitting parameters.

In a band-constant description of Λ-doubling splittings, individual Λ-doubling parameters $q_m^{(\alpha)}(v)$ are determined for each vibrational level of each isotopologue, using a fit to the first line of Eq. (17). Otherwise, the Dunham-type expansion of Eq. (18) is used. As with the normal Dunham expansion of Eq. (2), first-order semiclassical quantum-number scaling means that only the isotopologue-1 expansion parameters $\{q_{l,m}^{(1)}\}$ need be specified or determined, with those for other isotopologues being defined by the mass-scaling relationship of Eq. (19). Of course, use of Eqs. (17) or (18) to describe the effect of Λ-doubling assumes that the perturbing state(s) giving rise to the perturbation is/are relatively distant (in energy). If this is not the case and local perturbations associated with level crossings occur, the present approach would yield poor fits for many lines, and deperturbation methods should be used.

2.5. Treatment of spin splittings in $^2\Sigma$ states

In $^2\Sigma$ state molecules, the quantum-number label J is normally used for the total angular momentum, which is the vector sum of the spin ($\vec{S}$) and nuclear rotation ($\vec{N}$) angular momenta, $\vec{J} = \vec{N} + \vec{S}$. In this case, a decoupling of the spin angular momentum from the internuclear axis which increases with N gives rise to N-dependent shifts of the e and f parity components of a given rotational level. If the N-

independent component of such perturbations is subsumed into the vibrational level energy, the resulting energy shifts for levels of a $^2\Sigma^+$ state are may be written as [2,4,38]:

$$\delta E_\gamma^{(\alpha)}(v,N,e) = +(1/2)\,N \sum_{m=1} \gamma_m^{(\alpha)}(v)[N(N+1)]^{m-1}, \tag{20}$$

$$= +(1/2)\,N \sum_{m=1} \sum_{l=0} \gamma_{l,m}^{(\alpha)}(v+(1/2))^l[N(N+1)]^{m-1}$$

$$= +(1/2)\,N \sum_{m=1} \sum_{l=0} \gamma_{l,m}^{(1)}\left(\frac{\mu_1}{\mu_\alpha}\right)^{m+\frac{l}{2}}(v+(1/2))^l[N(N+1)]^{m-1}, \tag{21}$$

$$\delta E_\gamma^{(\alpha)}(v,N,f) = -(1/2)(N+1) \sum_{m=1} \gamma_m^{(\alpha)}(v)[N(N+1)]^{m-1}, \tag{22}$$

$$= -(1/2)(N+1) \sum_{m=1} \sum_{l=0} \gamma_{l,m}^{(\alpha)}(v+(1/2))^l[N(N+1)]^{m-1}$$

$$= -(1/2)(N+1) \sum_{m=1} \sum_{l=0} \gamma_{l,m}^{(1)}\left(\frac{\mu_1}{\mu_\alpha}\right)^{m+\frac{l}{2}}(v+(1/2))^l[N(N+1)]^{m-1}. \tag{23}$$

For $^2\Sigma^-$ states the e/f identity of Eqs. (20) and (21) interchange with those of Eqs. (22) and (23), respectively, but since **dParFit** does not carry or implement a quantum label to distinguish superscript $\pm$ states, all $^2\Sigma$ states are treated as $^2\Sigma^+$ in the code. While some conventions would label the present e and f states as F_1 and F_2, respectively, the language of program **dParFit** is based on the rotational state labelling appropriate for singlet states, so it uses only e and f. Similarly when discussing $^2\Sigma$ states, the label J used and/or printed by the program really means N. Note, however, that (in contrast with Λ-doubling) the isotopologue-mass dependence of the spin-rotation splitting Dunham-type expansion parameters is the same as that for Dunham $Y_{l,m}^{(\alpha)}$ coefficients:

$$\gamma_{l,m}^{(\alpha)} = (\mu_1/\mu_\alpha)^{m+l/2} \gamma_{l,m}^{(1)} \tag{24}$$

dParFit structurally identifies $^2\Sigma$ states as a special "$\Lambda = -2$" case of Λ-doubling. Thus, to identify state "s" as having $^2\Sigma$ symmetry, the parameter IOMEG(s) input through READ statement [#]5 should be given the value IOMEG(s) $= -2$. The representation of the spin-rotation parameters in band-constant format (Eqs. (20) and (22)) or Dunham-type format (Eqs. (21) and (23)) format, is then specified in exactly the same way, and by exactly the same control parameters and input READ statements ([#]32–36) used for Λ-doubling in singlet states. However, $^2\Sigma$ splitting parameters are identified appropriately in the output.

A final point here concerns the fact that in some spectra the $^2\Sigma$ splitting may not be resolved, or it may be resolved only for higher J (i.e., higher N) levels. One could treat this situation indirectly by inputting duplicate entries for the unsplit low-N lines, one with each parity label. However, this artificial duplication of data would give an incorrect relative weight for observations of the associated J (i.e., N) level, and would incorrectly imply that the splitting was experimentally determined to be identically zero. While that type of treatment is possible with **dParFit**, the recommended approach is to avoid introducing duplicate assignments, and instead to give the parity label $p = 0$ to

levels associated with any such unresolved transitions (as compared to $p = +1$ for e levels and $p = -1$ for f). This will cause **dParFit** to simply ignore spin-rotation contributions to the associated level energies.

2.6. Representations for Born–Oppenheimer Breakdown (BOB) terms

The validity of the simple first-order semiclassical reduced-mass scaling of Eq. (3) and of the analogous relationships for NDEs and Λ–doubling expansion coefficients rests on two assumptions: (i) that different isotopologues of a molecule in a given electronic state experience exactly the same effective internuclear potential energy function and (ii) that the first-order JWKB approximation and the associated Bohr–Sommerfeld quantization condition are exact. While both are fairly good approximations, neither is exactly true, and discrepancies due to their breakdown grow with decreasing mass of the component atoms. In particular, it has long been known that the third-order JWKB approximation introduces correction terms which scale as $(1/\mu_\alpha)$ [5,24,40], and that the leading corrections to the interaction potential between atoms A and B with (atomic) masses M_A and M_B due to the breakdown of the "clamped-nuclei" version of the Born–Oppenheimer approximation scale as $1/M_A$ and $1/M_B$, respectively [41–47]. In empirical fits of parameterized level-energy expressions to experimental data, these two types of corrections cannot be distinguished from one another. Moreover, as their effect depends on the differences between isotopic atomic masses [3], such terms can only be delineated when treating data for multiple isotopologues simultaneously in a unified analysis.

Following the approach of Ref. [3], **dParFit** collectively identifies the additive atomic-mass-dependent Born–Oppenheimer and first-order JWKB breakdown contributions to level energies as "BOB terms", and represents them by the expression

$$\delta E_{BOB}^{(\alpha)}(v,J) = \sum_{m=0}\sum_{l=0}\left\{\frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}}\delta_{l,m}^A + \frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}}\delta_{l,m}^B\right\} \quad (25)$$

in which $\Delta M_A^{(\alpha)} = M_A^{(\alpha)} - M_A^{(1)}$ is the difference between the mass of the isotope of atom-A in isotopologue-α from that in the reference species, isotopologue-1, and similarly for atom-B. This expression has a different algebraic form than one introduced by Ross et al. [48], which was subsequently theoretically justified by Bunker [44] and Watson [45]. However, the two are formally equivalent, and Eq. (25) has a number of important advantages [3]. One of these is the fact that the Ross–Bunker–Watson formulation [44,45,48] may only be applied if Dunham expansions are used for the vibration–rotation energies, while the additive terms of Eq. (25) can be combined equally readily with Dunham or NDE or MXS or any other analytic representations of the reference-isotopologue vibration–rotation level energies.

Note that as discussed in Ref. [3], the numerical values of the BOB correction parameters $\delta_{l,m}^A$ and $\delta_{l,m}^B$ depend on the choice of the reference isotopologue. Relative isotopologue abundances often make that choice obvious and

definitive. However, in the unusual case when one might wish to change the definition of reference isotopologue, the conversion of a set of fitted $\{\delta_{l,m}^A\}$ and $\{\delta_{l,m}^B\}$ values to the new choice of reference species (say, $\alpha = 2$) is quite straightforward, since following Ref. [3],

$$\delta_{l,m}^A(2) = \delta_{l,m}^A(1)[M_A^{(1)}/M_A^{(2)}] (\mu_1/\mu_2)^{m+l/2}, \quad (26)$$

and similarly for atom-B. Moreover, these recommended BOB parameters $\{\delta_{l,m}^A\}$ are simply related to the $\{\Delta_{l,m}^A\}$ parameters of the Ross–Bunker–Watson formulation [44,45,48] by the expression [3]:

$$\Delta_{l,m}^A = \delta_{l,m}^A [M_A^{(1)}/m_e] / [Y_{l,m}^{(1)} + \delta_{l,m}^A + \delta_{l,m}^B] \quad (27)$$

The presence of the factors $\Delta M_A^{(\alpha)}$ and $\Delta M_B^{(\alpha)}$ in Eq. (25) clearly mean that $\delta E_{BOB}^{(\alpha=1)}(v,J) \equiv 0$; i.e., by definition, BOB corrections do not contribute to the level energies of the species chosen as the reference isotopologue. However, if $\alpha > 1$ (i.e., for "minor" isotopologues) and Dunham expansions are used for the vibration–rotation energy, Eq. (25) may be combined with Eq. (2) to give the unified Dunham-type level-energy expression

$$E_{vJ}^{(\alpha)} = \sum_{l=0}\sum_{m=0} Y_{l,m}^{(\alpha)} (v+1/2)^l \left[J(J+1) - \Lambda^2\right]^m$$

$$= \sum_{l=0}\sum_{m=0}\left\{Y_{l,m}^{(1)} + \frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}}\delta_{l,m}^A + \frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}}\delta_{l,m}^B\right\}$$

$$\times \left(\frac{\mu_1}{\mu_\alpha}\right)^{m+l/2} (v+1/2)^l \left[J(J+1) - \Lambda^2\right]^m \quad (28)$$

Note that these summations do include the $(l,m) = (0,0)$ term. Although $Y_{0,0}^{(1)} \equiv 0$, $\delta_{0,0}^A$ and $\delta_{0,0}^B$, and hence also $Y_{0,0}^{(\alpha)}$ for $\alpha \neq 1$, may in general be non-zero. For multiple-isotopologue Dunham-fit analyses involving BOB corrections in which the fitted parameters are $\{Y_{l,m}^{(1)}\}$, $\{\delta_{l,m}^A\}$ and $\{\delta_{l,m}^B\}$, **dParFit** also reports the derived isotopologue-specific and BOB–corrected $\{Y_{l,m}^{(\alpha)}\}$ values of Eq. (28), and their uncertainties.

In principle, one might consider applying this same type of atomic-mass dependent BOB-type correction to the expressions for the Λ–doubling or $^2\Sigma$ splittings of Eqs. (17)–(23). However, in most cases such effects would be small corrections to small corrections, and the currents version of **dParFit** does not offer this option.

Eq. (25) may also be used to represent BOB terms when NDE or MXS functions are used to represent G_v and B_v. However, since the NDE approach "counts down" from $v_{\mathfrak{D}}^{(\alpha)}$ rather than counting up from $v = -1/2$, one ideally should also allow for BOB corrections to the effective vibrational index at dissociation. By analogy with Eq. (25), such atomic-mass dependent BOB corrections to $v_{\mathfrak{D}}^{(\alpha)}$ could be introduced by the expression

$$v_{\mathfrak{D}}^{(\alpha)} + 1/2 = \sqrt{\mu_1/\mu_\alpha}\left(v_{\mathfrak{D}}^{(1)} + 1/2\right) + \left(\frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}}\right)\delta v_{\mathfrak{D}}^A$$

$$+ \left(\frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}}\right)\delta v_{\mathfrak{D}}^B \quad (29)$$

which involves the two additional BOB correction parameters $\delta v_{\mathfrak{D}}^A$ and $\delta v_{\mathfrak{D}}^B$. However, Eq. (29) *is not implemented*, in the current version of **dParFit**.

2.7. Direct fits to term values $\{T^{(\alpha)}(v,J,p)\}$

In addition to the four ways of representing level energies described in Section 2.2, **dParFit** also allows the levels of a given state to be represented using an independent fitted term value $T^{(\alpha)}(v,J,p)$ for each observed (v,J,p) level of each isotopologue, an approach that was first developed by Åslund [49,50]. This approach is useful if levels of the state in question are sufficiently heavily perturbed that a smooth polynomial-type representation of their dependence on v and J cannot readily be obtained. If the analysis utilizes transitions from such a state to a more regular state, this approach allows an optimal compact parameterized description of the regular state to be obtained without contamination from problems associated with the representation of the perturbed state.

In early versions of **dParFit** this option could only be implemented indirectly for a second or higher electronic state, and it required all of the band data involving that (perturbed) state to be arranged into the input format designed for fluorescence series data, while the levels of the regular state were represented in a more conventional manner (by band constants or Dunham expansions, etc.). That approach was applied in successful data analyses for BaO, CaO and SrO [51–53]. However, in that approach it is difficult to discern trends in the [calc.-, obs.] differences obtained from the fits. In more recent versions of **dParFit** (Versions 3.2 and later) this option could be implemented for one (or more) electronic states without any re-arrangement of regular band data, simply by identifying the that/those states by giving the input parameter specifying how their vibrational energies were to be represented the value NDEGv $= -2$.

A critical condition associated with the use of this option is that all of the levels involved in the analysis must form a "connected set". If one is dealing only with electronic transitions in which (say) the upper state is represented by term values and the lower one by Dunham expansions, no problems will arise, as all the levels of the lower state would be interconnected by the Dunham expressions, which in turn indirectly connects all those upper-state levels to one another. On the other hand, if one adds to that data set a number of microwave transitions in the upper (term-value) state which had no levels in common with the electronic transitions, one would not have a "fully connected" set of data. A fit to such a data set would be analogous to attempting to determine two parameters from a single datum: **dParFit** would have computational under/overflows and the fit would yield "nan" ("not a number") complaints in place of values for fitted parameters. Another example of situation where this could occur is if one is fitting to vibrational Raman data for the ground electronic state of a homonuclear species such as H_2, for which transitions of the ortho (odd J) and para (even J) species have no levels in common.

If one is using some combination of Dunham, NDE or MXS representations for all of the states involved in a given analysis, the question of having a fully connected set of data does not arise, while if one is using a band-constant representation for the vibrational energies in one or more states, it may be explicitly addressed by specifying an appropriate value for the input parameter FITGV (see Read statement #8) for each vibrational level of that state. However, **dParFit** contains no automatic mechanism for testing or ensuring that the data input to a fit using a term-value representation comprises a fully connected set, so it is up to the user to ensure that this is the case.

2.8. T_0 vs. T_e, the $Y_{0,0}$ correction, and electronic isotope shifts

Finally, it is important for to specify clearly the convention that is being used to define the zero of energy and electronic isotope shift for a given electronic state. First of all, the energy zero of the first electronic state considered in the channel-5 instruction data file defines the energy zero of the overall analysis. If the vibrational energies of that first state are represented by band constants, then the rotationless energy of the lowest observed vibrational level of the reference isotopologue is the absolute zero of energy for the system. Similarly, if term values are used for that first state, its lowest observed vibration–rotation level defines that absolute energy zero. If the properties of any of the subsequent (second or third or further) states considered are represented either by band constants or by individual term values, the question of an overall energy zero for those states does not arise, as the energy of each vibrational (or vibration–rotation) level is treated independently. For this same reason, the question of overall electronic isotope shifts does not arise for states whose level energies are represented by either band constants or sets of term values.

For the three other types of vibrational energy representations, Dunham, pure NDE and MXS functions, the extrapolated vibrational energy of the reference isotopologue at $v = -1/2$ is defined as the reference energy $T_e \equiv T^{(\alpha = 1)}_{v=-1/2}$ for each electronic state [54]. Although this is an extrapolated quantity rather than the energy of an observable level, it is a simple matter to calculate the zero-point energy and hence to locate the zero-point level for any isotopologue using any of these analytic vibrational level energy expressions. Note that this definition of T_e *does not* include the Dunham-type zero-point energy corrections $Y^{(\alpha),sc}_{0,0}$ associated with breakdown of the first-order semiclassical quantization condition (see below) [5,2,55].

If breakdown of the Born–Oppenheimer approximation and of the first-order semiclassical quantization condition are neglected, then the electronic energy of a given electronic state $T_e \equiv T^{(\alpha)}_{-1/2}$ at $G^{(\alpha)}_{v=-1/2}$ is exactly the same for all isotopologues. This is a fairly good approximation for molecules formed from relatively heavy atoms. Moreover, our definition of BOB corrections in terms of the factors $\Delta M^{(\alpha)}_A / M^{(\alpha)}_A$ and $\Delta M^{(\alpha)}_B / M^{(\alpha)}_B$ means that such corrections are always defined to be identically zero for the reference isotopologue $\alpha = 1$. However, as discussed in Section 2.6, these approximations are never truly exact, and their breakdown must be considered in treatments of high-resolution multiple-isotopologue data sets.

dParFit represents the combined effect of the electronic isotope shift and the breakdown of the first-order semiclassical quantization condition by the leading BOB coefficients $\delta_{0,0}^A$ and $\delta_{0,0}^B$ of Eqs. (25) and (28), which yield the additive "apparent" electronic isotope shift

$$\delta T_{-1/2}^{(\alpha)} = \frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}} \delta_{0,0}^A + \frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}} \delta_{0,0}^B \qquad (30)$$

to the energies of all vibration–rotation levels of isotopologue α in the given electronic state. However, for the first state considered (in general, the lowest state), or if one is treating data involving only a single electronic state, the coefficients $\delta_{0,0}^A$ and $\delta_{0,0}^B$ cannot be determined empirically unless one is fitting to an MXS or pure NDE expression and the data are sufficiently extensive and sufficiently accurate to allow the fit to determine the differences between the well depths for different isotopologues of that state. When this is not the case, the isotope shift determined by **dParFit** for electronic state s_2 is actually an effective value defined as the difference between its absolute shift and that for the first electronic state considered, s_1:

$$\tilde{\delta T}_{-1/2}^{(\alpha)}(s_2) = T_{-1/2}^{(\alpha)}(s_2) - T_{-1/2}^{(\alpha)}(s_1) \qquad (31)$$

In this case the sum in Eq. (25) should *exclude* the $(l, m) = (0, 0)$ term for the first (lowest) electronic state considered in the analysis, but *include* it for all higher electronic states. This in turn means that the $\delta_{0,0}^{A/B}$ parameters determined by **dParFit** for the excited state would actually be the *differences* relative to the unknown values for the first (lowest) states

$$\tilde{\delta}_{0,0}^A(s_2) = \delta_{0,0}^A(s_2) - \delta_{0,0}^A(s_1) \qquad (32)$$

and similarly for atom-B, where by definition $\tilde{\delta}_{0,0}^A(s_1) \equiv 0 \equiv \tilde{\delta}_{0,0}^B(s_1)$ (see e.g., Ref. [56]).

The absence of sufficiently extensive and accurate multi-isotopologue data means that the electronic isotope shifts and parameters determined in most analyses will be the differences shown in Eqs. (31) and (32), with such terms for the first (lowest) state being by definition $\equiv 0$. However, **dParFit** can also treat unusual cases in which significant values of $\delta_{0,0}^A$ and/or $\delta_{0,0}^B$ can in fact be determined for the first (lowest) state. This option is invoked by giving the input parameter BOB00, which is read in (see READ #37) if BOB corrections are to be included for the first electronic state considered, the value BOB00 = 1.

2.9. Generating sets of predicted transition energies

A capability introduced in recent versions of **dParFit** (Versions 3.2 and later) is the ability to generate a set of data predictions $\{y_{\text{calc}}(i)\}$ from a given fixed set of input parameters. This option is invoked by setting the value of the input variable in Read #2, which is normally the name of the file containing the experimental data, to be "MAKEPRED". In this case the program will use Read #41 in the Channel-5 instruction data file to read specifications and selection rules for the bands for which the user wishes

to generate predictions, and the resulting predictions are written to file filename.8.

3. Using dParFit

3.1. Units, uncertainties and rounding

All input or output parameters associated with **dParFit** are either dimensionless or have units of energy. For the latter, any choice is possible as long as *all* input data and *any* read-in parameters use the same units (whether they be cm^{-1}, GHz, kHz, meV, or anything else); the output parameters will then be in those same units. This simplicity with units is one convenient feature of the formulation for the of BOB energy shift corrections that is used in **dParFit** [3].

The only physical constants required by **dParFit** are the atomic masses used to define the reduced mass of each isotopologue, and the electron mass, all in atomic mass units. The electron mass is required because for molecular ions the reduced mass actually used by **dParFit** is Watson's "charge-modified reduced mass" [45], which takes account of the loss or gain of one or more electrons on forming a molecular ion:

$$\mu_\alpha = M_A^{(\alpha)} M_B^{(\alpha)} / \left(M_A^{(\alpha)} + M_B^{(\alpha)} - m_e \times \text{CHARGE} \right), \qquad (33)$$

in which m_e is the mass of the electron, and "CHARGE" is the $\pm$ integer charge on the molecular ion. The value of the electron mass used in the program was taken from the 2010 CODATA recommended physical constant values [57], while the masses of all stable atomic isotopes stored in data subroutine MASSES were taken from the 2012 compilation of Ref. [58], so all a user need specify in the input is the atomic number and mass number of each atom of each isotopologue considered in the analysis.

Because **dParFit** performs weighted least-squares fits, each input datum must be accompanied by an uncertainty $u(i)$, with the same units as the observable. The quality of a fit of an M-parameter model to N input data which yields the predicted quantities $\{y_{\text{calc}}(i)\}$ is indicated by the value of the dimensionless root-mean-square deviation

$$\text{DRMSD} \equiv \overline{dd} = \left\{ \frac{1}{N} \sum_{i=1}^{N} \left[\frac{y_{\text{calc}}(i) - y_{\text{obs}}(i)}{u(i)} \right]^2 \right\}^{1/2}, \qquad (34)$$

or by the dimensionless standard $\text{DSE} \equiv \overline{\sigma}_f = \sqrt{N/(N-M)} \times \overline{dd}$. This data weighting allows observables with very different magnitudes and very different absolute uncertainties (e.g., microwave *vs.* electronic fluorescence data) to be treated concurrently in an appropriate balanced manner. A "good" fit is one which yields DSE and DRMSD values close to unity, since an DRMSD value of (say) 2.7 would mean that on average the predictions of the model disagree with the input data by 2.7 times the estimated experimental uncertainties.

In addition to reporting the 95% confidence limit (or "two-sigma") uncertainty in each fitted parameter, **dParFit** follows the approach of Ref. [59] by always also listing the associated "parameter sensitivity" (identified as PS in the

output). This quantity is defined (see Eq. (4) of Ref. [59]) as the magnitude of the largest change in the given parameter whose effect on the predictions of the model could increase $\overline{\sigma}_f$ by a maximum of $(0.1/M)\overline{\sigma}_f$. The parameter sensitivity indicates the degree to which any particular fitted parameter value may be rounded off while having no significant effect (within the data uncertainties) on the ability of the resulting parameter set to accurately predict the input data. For the illustrative cases considered in Ref. [59], to three significant digits rounding off all parameters at the first significant digit of their sensitivity had no significant effect on the values of $\overline{\sigma}_f$ or $\overline{dd}$.

Another feature of **dParFit** is its implementation (via subroutine NLLSSRR) of the automated "sequential rounding and refitting" (SRR) procedure of Ref. [59], which minimizes the total number of significant digits required to represent the overall parameter set with no (significant) loss of accuracy. Application of this procedure involves a substantial increase in computational effort relative to that required for an ordinary fit, so it is usually not desirable to use it in the many preliminary trial fits involved in any overall data analysis. Application of this procedure is turned on or off by the value of the flag IROUND which is set by the user in the input data file. One would normally turn this flag off (set IROUND=0) for preliminary analyses, and only turn it on when one wishes to generate a final parameter set to report and distribute. As discussed in Ref. [59], in most cases setting IROUND $= \pm 1$ yields a maximum degree of rounding without significant loss of precision, but in some cases it may be necessary to set |IROUND| > 1.

Although the only parameters determined directly in fits of multiple-isotopologue data to Dunham expressions are those for the chosen reference isotopologue $\alpha = 1$, **dParFit** uses Eq. (28) to generate the overall Dunham coefficients for the "minority" ($\alpha > 1$) isotopologues. However, the parameter rounding for the minority isotopologues must be based on the more conservative parameter-sensitivity criterion (see Ref. [56]), since the SRR procedure can only be applied to the parameters explicitly varied in the fits, and not to quantities derived from them. The uncertainties in those calculated minority-isotopologue effective Dunham parameters depend on those of both $\{Y_{l,m}^{(1)}\}$ and of $\{\delta_{l,m}^A\}$ and $\{\delta_{l,m}^B\}$, and they are calculated by **dParFit** using the correlation matrix for the fit and Eq. (7) of Ref. [59] (see, e.g. the "HF/DF" results in Table 1 of Ref. [3]).

One final choice regarding the manner in which the least-squares fits are performed is whether or not to perform "robust" fits. As described in Ref. [60] and references therein, *robust* least-squares fits attempt to minimize the effect of data "outliers", observations which yield anomalously large discrepancies with the model. When this choice is invoked, **dParFit** adopts the approach of Ref. [60] and replaces the normal least-squares data weights $w_i = 1/[u(i)]^2$ by the "*robust*" weights $w_i^{rob} = 1/([u(i)]^2 + [y_{calc}(i) - y_{obs}(i)]^2/3)$. Because the latter depend on the then-current degree of agreement of the data with the model, fits of this type are repeated iteratively, with the parameter values and the weights being updated in each cycle until self-consistency is achieved. As a result, *robust*

fits require substantially more computer time than do normal fits. Moreover, the fact that *robust* weighting reduces the effect of large $[y_{calc}(i) - y_{obs}(i)]$ values on DSE and DRMSD makes it more difficult to interpret differences in those quantities obtained from fits to different version of a model, and it may tend to obscure the presence of systematic discrepancies which indicate shortcomings of the model, rather than of the data. The author's limited experience with this option indicates that it can be very useful for examining data sets both for local irregularities and for systematic discrepancies from a model by examining the [calc. − obs] results in the channel-8 output file. However, I would recommend *not* using the *robust* option when determining a final recommended set of parameters.

3.2. Array dimensions, input/output conventions, and program execution

The operation of program **dParFit** involves the use of a number of moderately large multi-dimensional integer and real-number arrays whose size is specified at the time the program is compiled. If those arrays are unnecessarily large, it could slow or hinder computations on some computers. In order to accommodate for the possible use of a Fortran-77-type compiler, which does not allow run-time array dimensioning, the current version of **dParFit** assumes that array dimensions must be set up when the code is compiled. Thus as one does not wish to have to recompile the code case-by-case, setting those array dimension at modest (but adequate) values should facilitate computations by minimizing computer memory requirements. Parameters that place upper bounds on the sizes of the large arrays are set by PARAMETER statements contained in the Block Data subroutine arrsizes.h found at the beginning of the the file containing the listing of the Fortran code in the Supplementary Material. The limits defined there are: the maximum number of isotopologues being considered, NISTPMX (currently set at 10), the maximum number of electronic states, NSTATEMX (currently set at 5), the maximum number of fitting parameters, HPARMX (currently 3000), the maximum number of data that the code can handle, NDATAMX (currently 22 000), as well as the maximum order l_{max} allowed in the Dunham expansions of Eqs. (2), (4) and (5) or in the NDE polynomial expansion parameters of Eqs. (11) and (12), NDUNMX (currently 20), the maximum number of observed vibrational levels in any of the electronic states considered NVIBMX (currently 155), and the maximum number of rotational (J or N) values for a given vibrational level (a number required for term-value-fit parameter counting) NVIBMX (currently 200), A user should examine these limits and ensure that they suffice for the analysis that they wish to pursue before compiling the code. Note that if a particular application requires a user to set HPARMX > 3000 (term-value fits can require *many* parameters), the value of parameter MXPdim that is set by a PARAMETER statement at line [#]7196 of the source code must also be reset to that new larger value.

dParFit reads two separate input data files, one which contains all of the raw experimental data, and one which contains the flags and control parameters that characterize

the problem and specify what type of fit is to be performed. The structure of these data files and the definitions of and options for the various input quantities are presented in Appendices A and B in the Supplementary Material.

The program writes standard output to Channel-6 and supplementary output files to Channels 7–10. The standard output written to Channel-6 summarizes the input data, describes the nature of the fit being performed, reports the results of the fit, lists fitted parameters and their sensitivities and their (95% confidence limit, or "two-sigma") uncertainties, and presents a summary of the $[y_{calc}(i) - y_{obs}(i)]$ results. The Channel-7 output file contains values of the band constants for all levels of all isotopologues of all states involved in the analysis, as generated from the final results of the fit. The Channel-8 output file contains a listing of the $\{[y_{calc}(i) - y_{obs}(i)]\}$ and $\{[y_{calc}(i) - y_{obs}(i)]/u(i)\}$ values for all data used in the fit. For the convenience of LATEX users, for multi-isotopologue Dunham-type fits the Channel–9 output file contains a listing of the final fitted parameters and of the predicted (and sensitivity-rounded) minority-isotopologue parameters with their names given in proper LATEX format. Finally, the Channel–10 output file contains the correlation matrix associated with the fit. All of these output files share the common root name WRITFILE which is input via Read #3 with a suffix defined by the Channel number. For example, if the input value of WRITFILE is, say, BeO-dun65331, the output files would be BeOdun65331.6, BeOdun65331.7, BeOdun653 31.8, etc. This grouping of output for a give case in a family of files with related filenames greatly facilitates user book-keeping.

Those executing **dParFit** in a UNIX or LINUX operating system environment may find it convenient to do so using a shell named (say) rdpar, such as that shown below, which may be stored in the system or user's "bin" directory:

```
#!/bin/sh
# UNIX shell 'dpar' to execute the compiled version of program {\bf dParFit} named
#   dpar.x, which is stored in the user directory /userpath/parfit/. The
#   Channel-5 input data file  $1.5  and the output files WRITFILE.6,
#   WRITFILE.7, ... etc., will be in the same directory.

time /userpath/dpar.x  < $1.5
```

in which userpath is a path specifying the location of the executable file dpar.x on the user's computer. This shell allows the program to be executed with the simple command:

```
rdpar filename
```

in which filename.5 is the data file containing the instructions regarding the type of fit to be performed; filename may be any name chosen by the user, but it is usually convenient if it has a name which identifies the particular case. If this file does not reside in the current directory, this name must, of course, also include the relative path.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2016.04.004.

Supplementary material associated with this paper consist of: a text file containing the full standalone Fortran source code for program **dParFit**, a text file containing the sample data files that are presented in Appendix C, and a document containing: (i) Appendix A, a detailed illustrated description of the manner in which the various types of experimental data are to be arranged in the input data file, whose name is input through Read #2 of the Channel-5 "instruction" input file, (ii) Appendix B.1, a structured listing of the Read statements used in the program, (iii) Appendix B.2, full definitions of all of the parameters and quantities read in the input "instruction" data file, and descriptions of the associated program options, (iv) Appendix C, commented listings of illustrative sample input and output files for three cases, and (iv) Appendix D – an overview of the program structure. Note that the Equation and reference numbering appearing in this Supplemental Material document refer to those in this Journal article, so for completeness we hereby reference six papers referenced there that are associated with particular applications of this code, but had not been referred to above [61–66].

Anyone who wishes to be Registered with the author as a user of this code, eligible to be sent any future bug fixes or updates, should fill in the online form at the www address http://www.scienide2.uwaterloo.ca/~rleroy/dParFit16.

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$Y_{0,0} = (Y_{0,1} + Y_{2,0})/4$
$-[(Y_{1,1} \ Y_{1,0})/(12 \ Y_{0,1})] + [(Y_{1,1} \ Y_{1,0})/(12 \ Y_{0,1})]^2/Y_{0,1}$, and that the relation $Y_{l,m} \equiv \frac{\partial^l}{\partial v^l} \frac{\partial^m E(v,J)}{\partial [J(J+1)]^m}|_{J=0,v=-1/2}$ allows this expression to be applied to any analytic representation for the vibration–rotation energies. DParFit uses these derivative relations to generate values of the conventional low-order constants ω_e, $\omega_e x_e$, B_e and α_e (and their uncertainties) associated with NDE or MXS level-energy representations.

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