DParFit 3.3
A Computer Program for Fitting Diatomic Molecule Spectral Data to Parameterized Level Energy Expressions

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This manual 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 vibrational bands, fluorescence series, binding energies (from photo-association spectroscopy) or values of the inertial rotational constant B_v. The level energies for each electronic state may be described by one of: (i) band constants $\{G_v,\ B_v,\ D_v,\ ...$ etc.$\}$ for each vibrational level, (ii) generalized Dunham expansions, (iii) pure near-dissociation expansions (NDE), (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.

I.   INTRODUCTION

In recent decades, the increasing sophistication, accuracy and productivity of experimental methods have 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 still tends to focus on isolated individual 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 allows simultaneous fits to any combination of microwave, infrared or electronic vibrational bands, photoassociation spectroscopy binding energies, fluorescence series, or inertial rotational constants B_v, involving one or more singlet or $^2\Sigma$ electronic states and one or more isotopologues. The levels for each electronic state may be represented in a variety of ways (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 II describes the level energy expressions which may be fitted to, and outlines some of the program's options. Section III 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 specifies the nature of the system and 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 Section IV. Finally, the Appendices outline the structure of the program and the roles of its various subroutines, and presents (partial) listings of illustrative output files.

The current version of the extensively commented source code for DParFit (an acronym for **$\boldsymbol{D}$**iatomic **$\boldsymbol{Par}$**ameter **$\boldsymbol{Fit}$**ting) may be obtained by filling in the appropriate form on the "DParFit" link from the "Computer Programs" link on the www page *http://leroy.uwaterloo.ca*; a PDF file of this manual is also available there. While, there are no charges associated with distribution or use of this program, its use should be acknowledged in publications through reference to this report using a citation such as that of Ref. 1.[1–3] Users are also requested *not* to distribute the program themselves, but to refer other prospective users to the above web site or to the author. I would also appreciate having users inform me of any apparent errors or instabilities in the code, and of additional features which might appear desirable for future versions.

II.   THEORETICAL BACKGROUND, EXPRESSIONS USED, AND PROGRAM OPTIONS

A. General Considerations, and Treatment of Multiple Isotopologues

For each electronic state the parameters representing the level energies are divided into five groups, for most of which one can make different choices of the type of representation to be used. The first group describes the vibrational energies G_v, the second the inertial rotational constants B_v, and the third the centrifugal distortion constants $\{D_v,\ H_v,\ ...\ \text{etc.}\}$. The fourth group is concerned with the Lambda doubling constants for electronic states with $\Lambda > 0$ (or for Hund's case–c coupling,[4] with $\Omega \neq 0$), or with the analogous constants characterizing spin-rotation splitting in $^2\Sigma$ states, and the fifth is the set of parameters defining atomic-mass-dependent terms characterizing the breakdown of the Born-Oppenheimer approximation and the first-order semiclassical (or JWKB) approximation, which are collectively called "BOB" corrections.

In the expressions for these quantities given below, the label α is used to identify a particular iso-topologue of the system. The fact that DParFit is designed for (but not restricted to) treating multiple-

isotopologue data sets means that most parameter symbols include the subscript or superscript label "α". This introduces some clutter to the notation, but 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 labeled $\alpha = 1$; 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 II.F). As discussed in Ref. 5, this reference isotopologue would usually be chosen to be the most abundant isotopologue, since intensity considerations mean that the most extensive (in v and J) data sets are usually available for that species. However, a user can 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,[6] 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. The ability to take account of $^2\Sigma$ level splittings (see §II.E) is a feature initially introduced in the Version 3.2 of this code.

B. Representations for G_v and for B_v

The first four methods of representing level energies described here all assume their explicit partitioning into a distinct vibrational energy plus separate terms representing different orders 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 II.G. DParFit allows a user to choose among four possible ways of representing the vibrational energies G_v and the inertial rotational constants B_v.

1. Band Constant Expressions

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

$$
\begin{aligned}
E^{(\alpha)}(v, J) &= \sum_{m=0} K_m^{(\alpha)}(v) \, [J(J+1) - \Lambda^2]^m \\
&= G_v^{(\alpha)} + B_v^{(\alpha)} \, [J(J+1) - \Lambda^2] - D_v^{(\alpha)} \, [J(J+1) - \Lambda^2]^2 + H_v^{(\alpha)} \, [J(J+1) - \Lambda^2]^3 + ... \quad (1)
\end{aligned}
$$

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 would be constrained to yield a single set of consistent constants for that level. 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's to be represented by Dunham, NDE or MXS expansions (see below) while the rotational constants (B_v's and/or centrifugal distortion constants) are represented by band constants. However, if G_v's are to be represented by band constants, the same must be true for all rotational constants. Similarly, if B_v's are treated as band constants (when the G_v's are not), the same must be true for the CDC's.

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,[4,7]

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

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 reduced mass of isotopologue–α (see Section III). 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 $Y_{0,0}^{(\alpha)} \equiv 0$. Corrections to these approximations are discussed in Section II.F. For G_v and B_v the resulting Dunham expansions are therefore

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

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

Note that the parameter values $Y_{l,m}^{(\alpha)}$ for the different isotopologues are not independent of one another, but are defined by the values for isotopologue–1 and the respective reduced masses (see Eq. (3)). Thus, independent of the number of isotopologues considered simultaneously, the only "free" parameters are those ($\{Y_{l,m}^{(1)}\}$) for the selected reference isotopologue, $\alpha = 1$.

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[8–11] in an expression which includes empirical parameters to be determined from the experimental data.[12–15] 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, and hence are much more effective for extrapolating to high v beyond the range of observed data[13,14,16] and for compactly representing data sets spanning a large fraction of the potential well.[12,15,17] The rest of this subsection discusses the use of NDE expressions and their parameterization in program DParFit; interested users may wish to review associated theory and review papers[8–11,14,18–20] and illustrative applications of this approach.[13,15,17,21–23]

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. As a result, their v-dependence is mainly determined by the limiting asymptotic behaviour of the intermolecular potential, which in most 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),[9,18] and reliable values of the limiting long-range coefficient C_n are often known from theory. 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

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

4

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 by

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

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

$$K_m^{(\alpha),\infty}(v) = (\mu_1/\mu_\alpha)^{[n/(n-2)]-m} X_m^{(1)}(n, C_n) \left(v_{\mathfrak{D}}^{(\alpha)} - v \right)^{[2n/(n-2)]-2m} \tag{9}$$

in which $X_m^{(1)}(n, C_n) = \bar{X}_m(n)/[(\mu_1)^n (C_n)^2]^{1/(n-2)}$ and $\bar{X}_m(n)$ is a known numerical factor depending only on the physical constants and the value of the integer n.[9,10,19] Normal first-order semiclassical mass scaling[7,24] interrelates the values of $v_{\mathfrak{D}}^{(\alpha)}$ for different isotopologues: $(v_{\mathfrak{D}}^{(\alpha)} + \frac{1}{2}) = \sqrt{\mu_1/\mu_\alpha} \left(v_{\mathfrak{D}}^{(1)} + \frac{1}{2} \right)$. The fitting 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

$$\mathcal{F}_m^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v) = \left(\frac{1 + \sum_{i=t}^{L} p_i^{(\alpha),m} \left(v_{\mathfrak{D}}^{(\alpha)} - v \right)^i}{1 + \sum_{j=t}^{M} q_j^{(\alpha),m} \left(v_{\mathfrak{D}}^{(\alpha)} - v \right)^j} \right)^{\mathcal{S}} \tag{10}$$

in which the exponent power $\mathcal{S}$ is set at either $\mathcal{S} = 1$ (to yield what is called an "outer" expansion) or $\mathcal{S} = 2n/(n-2)$ (yielding an "inner" expansion). For some cases, the most appropriate value of the leading expansion order t is known from theory.[25] The expansion parameters for different isotopologues α are related by the usual first-order semiclassical mass-scaling relationship: $p_i^{(\alpha),m} = (\mu_1/\mu_\alpha)^{i/2} p_i^{(1),m}$ and $q_j^{(\alpha),m} = (\mu_1/\mu_\alpha)^{j/2} q_j^{(1),m}$, and the numbers ($L + 1 - t$ and $M + 1 - t$, respectively) of empirical numerator and/or denominator coefficients $p_i^{(1),m}$ and $q_i^{(1),m}$ depend on the nature and extent of the data. 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

$$\mathcal{F}_m^{(\alpha)}(v_{\mathfrak{D}}^{(\alpha)} - v) = \exp\left\{ \sum_{i=t} p_i^{(\alpha),m} (v_{\mathfrak{D}}^{(\alpha)} - v)^i \right\} \tag{11}$$

in which the expansion parameters for different isotopologues α are again related by the simple first-order semiclassical mass scaling relationship, $p_i^{(\alpha),m} = (\mu_1/\mu_\alpha)^{i/2} p_i^{(1),m}$.

Although some properties of NDE expansions 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 selecting the particular choice of the power $\mathcal{S}$ and of the numbers of numerator ($L + 1 - t$) and denominator ($M + 1 - t$) expansion terms).[12,13,15,16] However, use of a (relatively) simple companion program GvNDE which automatically fits a given set of vibrational energies to all forms of Eq. (10) and (11) consistent with a given total number of expansion parameters and selected t value,[26] 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 for the non-linear least-squares fitting procedure.

While they are somewhat more complex 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 very 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,[25] also) of t appropriate to the particular molecular state,[9,18,20,25] (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[26] GvNDE to preliminary sets of vibrational energies or B_v values. 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 §II.F).

One further point unique to the use of NDE expansions 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. In DParFit, the value of $\mathfrak{D}$ for the first electronic state treated using an NDE (or MXS, see below) expression for G_v is treated as the free or defining dissociation-limit parameter, while those for other NDE-represented states are fixed relative to the first using the differences between the read-in (trial) dissociation limits.

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 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 the effects of finite precision roundoff would 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.[27,28] 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 nature 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.[28] This form uses

- a normal Dunham polynomial (see §II.B.2) for $v \lesssim v_s$ and
- a near dissociation expansion (see §II.B.3) for $v \gtrsim v_s$,

and merges the two at a chosen switch-over point $v = v_s$ using the switching function

$$F_s(v) \;\; = \;\; \left\{ 1 + \exp\left(\frac{v - v_s}{\delta v_s} \right) \right\}^{-1} \tag{12}$$

to yield the MXS expressions

$$G_v^{\mathrm{MXS}} \;\; = \;\; F_s(v)\, G_v^{\mathrm{Dun}} \;\; + \;\; [1 - F_s(v)]\, G_v^{\mathrm{NDE}} \tag{13}$$

$$B_v^{\mathrm{MXS}} \;\; = \;\; F_s(v)\, B_v^{\mathrm{Dun}} \;\; + \;\; [1 - F_s(v)]\, B_v^{\mathrm{NDE}} \tag{14}$$

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 physical ($\mathfrak{D}$ and $v_\mathfrak{D}$) and other parameters defining the NDE function, as well as values for the 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.[26] For "regular" (i.e., non-shelf) states, the method is 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 appropriate 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.[29] 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 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 at 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.

C. Representations for Centrifugal Distortion Constants (CDCs)

1. Three Choices for Representing 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, any Λ-doubling or $^2\Sigma$-splitting contributions are also fitted as band constants.

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

$$K_m^{(\alpha)}(v) \;\; = \;\; \sum_{l=0} Y_{l,m}^{(\alpha)} \, (v + \tfrac{1}{2})^l \;\; = \;\; \sum_{l=0} Y_{l,m}^{(1)} \, (\mu_1/\mu_\alpha)^{m+l/2} \, (v + \tfrac{1}{2})^l \tag{15}$$

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 (11). 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) CDCs (see, e.g., Fig. 5 of Ref. 17), 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 be expected to give rise to spurious oscillations or instabilities.

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,[30–32] which in turn is used in a quantal calculation[33–35] to compute "true" values of the CDC constants implied by that potential energy function. Holding the CDCs 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.[15,36,37] 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 CDCs 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,[11,14,19] NDE functions are in fact the *only* meaningful way of representing them analytically for levels approaching dissociation.[14,15,17] Note, however, that the only NDE expression for CDCs allowed by DParFit is the exponential form of Eq. (11), 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,[11,14,19] and it is also appropriate for all levels of some molecular states.[15,17] 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, D_v to O_v.[35] 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.

D. 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 $[J(J+1)]$.[38] Moreover, every rotational level is split into a doublet of e and f rotational parity states with a splitting proportional to $[J(J+1)]$, and the band-constant type coefficient determining its magnitude varies with isotopologue, with vibrational energy, and with the (mechanical) centrifugal distortion.[4,6] DParFit represents such splittings by an additive energy correction expressed using either a band-constant or a Dunham-expansion type of representation:

$$\delta E_\Lambda^{(\alpha)}(v, J, \{e/f\}) = \mathrm{sg}(\{e/f\})\,[J(J{+}1)]^\Lambda \sum_{m=\Lambda} q_m^{(\alpha)}(v)\,[J(J{+}1) - \Lambda^2]^{m-\Lambda} \tag{16}$$

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

$$= \mathrm{sg}(\{e/f\})\,[J(J{+}1)]^\Lambda \sum_{m=\Lambda}\sum_{l=0} q_{l,m}^{(1)}\left(\frac{\mu_1}{\mu_\alpha}\right)^{\Lambda+m+\frac{l}{2}}\,(v{+}\tfrac{1}{2})^l\,[J(J{+}1) - \Lambda^2]^{m-\Lambda} \tag{17}$$

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 $\mathrm{sg}(e) = +\frac{1}{2}$ and $\mathrm{sg}(f) = -\frac{1}{2}$. However, DParFit allows a user to make other choices for them.

As discussed in Refs. 6, 39 and 40, 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 Σ^+ or Σ^- state. If that perturbing state has Σ^+ 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 Σ^- 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 $\mathrm{sg}(e) = 0$ and $\mathrm{sg}(f) = -1$. 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. (16) and (17) 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.[39]

As shown by Eq. (17), the isotopologue mass-dependence of Λ–doubling splitting constants

$$q_{l,m}^{(\alpha)} = (\mu_1/\mu_\alpha)^{\Lambda+m+l/2}\, q_{l,m}^{(1)} \tag{18}$$

(recall that $m \geq \Lambda$) differs from that for the conventional rotational constants (see Eq. (3)) by additional power(s) of (μ_1/μ_α). 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.[40] 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 $\mathrm{sg}(e) = +1$ and $\mathrm{sg}(f) = 0$ in Eq. (17) rather than one of the two other choices. While such differences are expected to be fairly small, they should sometimes be observable. When this occurs, it means that the fit is able to identify the symmetry of the dominant perturbing state ($^1\Sigma^+$ vs. $^1\Sigma^-$) responsible for the splitting.[40] In any case, DParFit allows a user to study such questions by requiring them to select a particular $\mathrm{sg}(\{e/f\})$ convention when fitting to determine Λ–doubling splitting parameters.

In a band-constant description of Λ–doubling splittings, individual vibrational level Λ–doubling parameters $q_m^{(\alpha)}(v)$ are determined for each vibrational level of each isotopologue, using Eq. (16). Otherwise, the Dunham-type expansion of Eq. (17) 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. (18). Of course, use of Eqs. (16) or (17) 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.

E. 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 [4,6,39]

$$\delta E_\gamma^{(\alpha)}(v,N,e) = +\tfrac{1}{2}N \sum_{m=1} \gamma_m^{(\alpha)}(v) \, [N(N{+}1)]^{m-1} \tag{19}$$

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

$$= +\tfrac{1}{2}N \sum_{m=1} \sum_{l=0} \gamma_{l,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha}\right)^{m+\frac{l}{2}} (v+\tfrac{1}{2})^l \, [N(N{+}1)]^{m-1} \tag{20}$$

$$\delta E_\gamma^{(\alpha)}(v,N,f) = -\tfrac{1}{2}(N{+}1) \sum_{m=1} \gamma_m^{(\alpha)}(v) \, [N(N{+}1)]^{m-1} \tag{21}$$

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

$$= -\tfrac{1}{2}(N{+}1) \sum_{m=1} \sum_{l=0} \gamma_{l,m}^{(1)} \left(\frac{\mu_1}{\mu_\alpha}\right)^{m+\frac{l}{2}} (v+\tfrac{1}{2})^l \, [N(N{+}1)]^{m-1} \tag{22}$$

Note, however, that the language of the comments within program DParFit is based on the rotational state labeling appropriate for $^1\Sigma$ states, so when discussing $^2\Sigma$ states, the label J used and/or printed by the program really means N. Note too 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:

$$\gamma_{l,m}^{(\alpha)} = (\mu_1/\mu_\alpha)^{m+l/2} \, \gamma_{l,m}^{(1)} \tag{23}$$

DParFit formally treats $^2\Sigma$ 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 (Eqs. (19) & (21)) or Dunham-type (Eqs. (20) & (22)) format, is then specified in exactly the same way and by exactly the same control parameters and input read statements ($^\#31-35$) used for Λ–doubling in singlet states. However, $^2\Sigma$ splitting parameters are labeled 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 observed line, 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.

F. 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) different isotopologues of a molecule in a given electronic state experience exactly the same effective internuclear potential energy function, and (ii) the first-order JWKB approximation and the associated Bohr-Sommerfeld

quantization condition are exact. While reasonably good approximations, neither of these assumptions 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 $(1/\mu_\alpha)$,[7,24,41] 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.[42–48] 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,[5] such terms can only be considered when treating data for multiple isotopologues simultaneously in a unified analysis.

Following the approach of Ref. 5, 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

$$\delta E_{\mathrm{BOB}}^{(\alpha)}(v,j) = \sum_{m=0}\sum_{l=0} \left\{ \frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}}\, \delta_{l,m}^A + \frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}}\, \delta_{l,m}^B \right\} \left(\frac{\mu_1}{\mu_\alpha}\right)^{m+l/2} (v+\tfrac{1}{2})^l\, [J(J+1)-\Lambda^2]^m \quad (24)$$

in which $\Delta M_A^{(\alpha)} = M_A^{(\alpha)} - M_A^{(1)}$ is the difference between the atomic mass of the isotope of atom–A forming isotopologue–α and that for the isotope of that atom found in the reference species, isotopologue–1 (similarly for atom–B). This expression has a different algebraic form than one introduced by Ross *et al.*[49], which was subsequently theoretically justified by Bunker[45] and Watson.[46] However, the two are formally equivalent, and Eq. (24) has a number of important advantages.[5] One of these is the fact that the Ross *et al.*[49] formulation may only be applied if Dunham expansions are used for the vibration-rotation energies, while the additive terms of Eq. (24) can be combined equally readily with Dunham or NDE or MXS or any other analytic representations of the isotopologue–1 vibration-rotation level energies.

Note that as discussed in Ref. 5, 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[5]

$$\delta_{l,m}^A(2) = \delta_{l,m}^A(1)\,[M_A^{(1)}/M_A^{(2)}]\,(\mu_1/\mu_2)^{m+l/2} \quad (25)$$

and similarly for atom–B. Moreover, these recommended BOB parameters $\{\delta_{l,m}^A\}$ are simply related to those of the Ross *et al.*[49] formulation by the expression[5]

$$\Delta_{l,m}^A = \delta_{l,m}^A\,[M_A^{(1)}/m_e] \Big/ [Y_{l,m}^{(1)} + \delta_{l,m}^A + \delta_{l,m}^B] \quad (26)$$

The presence of the factors $\Delta M_A^{(\alpha)}$ and $\Delta M_B^{(\alpha)}$ in Eq. (24) clearly mean that $\delta E_{\mathrm{BOB}}^{(\alpha=1)}(v,j) \equiv 0$; 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. (24) may be combined with Eq. (2) to give the single Dunham-type level-energy expression

$$E_{v,J}^{(\alpha)} = \sum_{l=0}\sum_{m=0} Y_{l,m}^{(\alpha)}\, (v+\tfrac{1}{2})^l\, [J(J+1)-\Lambda^2]^m \quad (27)$$

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

Note that these summations include the $(l,m) = (0,0)$ term; although $Y_{0,0}^{(1)} \equiv 0$, $\delta_{0,0}^A$ & $\delta_{0,0}^B$, and hence also $Y_{0,0}^{(\alpha)}$ for $\alpha \neq 1$, are in general 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. (27), 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. (16) – (22). However, in most cases such effects would be small corrections to small corrections, and the currents version of DParFit does offer this option.

Eq. (24) 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 $v = -\frac{1}{2}$, one should ideally also allow for BOB corrections to the effective vibrational index at dissociation. By analogy with Eq. (24), such atomic-mass dependent BOB corrections to $v_{\mathfrak{D}}^{(\alpha)}$ would be introduced by the expression

$$v_{\mathfrak{D}}^{(\alpha)} + \tfrac{1}{2} \;\;=\;\; \sqrt{\mu_1/\mu_\alpha}\,\left(v_{\mathfrak{D}}^{(1)} + \tfrac{1}{2}\right) + \left(\frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}}\right)\delta v_{\mathfrak{D}}^A + \left(\frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}}\right)\delta v_{\mathfrak{D}}^B \tag{28}$$

which involves the two additional BOB correction parameters $\delta v_{\mathfrak{D}}^A$ and $\delta v_{\mathfrak{D}}^B$. **_However,_** Eq. (28) **_is not implemented_** in the current version (3.3) of DParFit.

G. Direct Fits to Term Values $\{T^{(\alpha)}(v, J, p)\}$

In addition to the four ways of representing level energies described in § II.B, 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 first developed systematically by Åslund.[50,51] 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 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 or ... etc.). That approach was applied in data analyses for BaO, CaO and SrO.[52–54] However, in that approach it is difficult to discern trends in the [calc. - obs.] differences obtained from such fits. In the recent versions of DParFit (V. 3.2 & later) this option may be implemented for one (or more) electronic states without any re-arrangement of the data, simply by giving the input parameter specifying the treatment of the vibrational energies for that state 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.

H. T_0 vs. T_e , the $Y_{0,0}$ Correction, and Electronic Isotope Shifts

Finally, it is important for to specify clearly the convention which is 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 $T_e \equiv T_{v=-1/2}^{(\alpha=1)}$ for each electronic state.[55] 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 $Y_{0,0}^{(\alpha),\text{sc}}$ associated with breakdown of the first-order semiclassical quantization condition (see below).[4,7,56]

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 $T_e \equiv T_{-1/2}^{(\alpha)}$ at $G_{v=-1/2}^{(\alpha)}$ 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 $\Delta M_A^{(\alpha)}/M_A^{(\alpha)}$ and $\Delta M_B^{(\alpha)}/M_B^{(\alpha)}$ means that such corrections are always defined to be identically zero for the reference isotopologue $\alpha=1$. However, as discussed in §II.F, 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. (24) and (27), which yield the additive "apparent" electronic isotope shift

$$\delta T_{-1/2}^{(\alpha)} = \frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}} \delta_{0,0}^A + \frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}} \delta_{0,0}^B \tag{29}$$

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:

$$\widetilde{\delta T}_{-1/2}^{(\alpha)}(s_2) = T_{-1/2}^{(\alpha)}(s_2) - T_{-1/2}^{(\alpha)}(s_1) \tag{30}$$

In this case the sum in Eq. (24) 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* from the values for the first (lowest) states

$$\widetilde{\delta}_{0,0}^{A}(s_2) = \delta_{0,0}^{A}(s_2) - \delta_{0,0}^{A}(s_1) \tag{31}$$

and similarly for atom–B, where by definition $\widetilde{\delta}_{0,0}^{A}(s_1) \equiv 0 \equiv \widetilde{\delta}_{0,0}^{B}(s_1)$ (see e.g., Ref. 57).

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. (30) and (31), 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 $^{\#}$36) if BOB corrections are to be included for the first electronic state considered, the value `BOB00`$=1$.

III.   USING DPARFIT

A. Units, Uncertainties, 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 which is used in DParFit.[5]

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",[46] which takes account of the loss or gain of one or more electrons on forming a molecular ion:

$$\mu_\alpha = M_A^{(\alpha)} M_B^{(\alpha)} / \left(M_A^{(\alpha)} + M_B^{(\alpha)} - m_e \times \texttt{CHARGE} \right) \tag{32}$$

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 2002 compilation of Ref. 58 and the atomic isotope masses from the 1993 compilation of Ref. 59. For all stable isotopes of all atoms, these masses are stored in the data subroutine MASSES, 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 standard error

$$\texttt{DSE} \equiv \bar{\sigma}_f = \left\{ \frac{1}{N-M} \sum_{i=1}^{N} \left[\frac{y_{\text{calc}}(i) - y_{\text{obs}}(i)}{u(i)} \right]^2 \right\}^{1/2} \tag{33}$$

or by the dimensionless root mean square deviation $\texttt{DRMSD} \equiv \overline{\text{dd}} = \sqrt{(N-M)/N} \times \bar{\sigma}_f$. 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. 60 by always also listing the associated "parameter sensitivity" (identified as `PS` in the output). This quantity is defined (see Eq. (4) of Ref. 60) as the magnitude of the largest change in the given parameter whose effect on the predictions of the model could increase $\bar{\sigma}_f$ by a maximum of $(0.1/M)\,\bar{\sigma}_f$. 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. 60, to three significant digits rounding off all parameters at the first significant digit of their sensitivity had no significant effect on the values of $\bar{\sigma}_f$ or $\overline{dd}$.

Another feature of DParFit is its implementation (via subroutine NLLSSRR) of the automated "sequential rounding and refitting" (SRR) procedure of Ref. 60, 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. 60, 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 $|\text{IROUND}| > 1$.

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. (27) 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. 57), 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. 60 (see, e.g. the "HF/DF" results in Table 1 of Ref. 5).

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. 61 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. 61 and replaces the normal least-squares data weights $w_i = 1/[u(i)]^2$ by the '*robust*' weights $w_i^{\text{rob}} = 1/\left([u(i)]^2 + [y_{\text{calc}}(i) - y_{\text{obs}}(i)]^2/3\right)$. 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 $[y_{\text{calc}}(i) - y_{\text{obs}}(i)]$ 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.

B. 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. The current version of DParFit assumes (but does not require) the use of a Fortran-77 compiler, which does not allow run-time array dimensioning. Thus, while 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 which place upper bounds on the sizes of the large arrays are set by PARAMETER statements contained in the utility routine arrsizes.h which is supplied with the

program. If this file resides in the same directory as the source code when the program is being compiled, most FORTRAN compilers will automatically incorporated it into relevant subroutines at compilation time through FORTRAN `include` statements in the code. Parameters defined in this way include the maximum number of isotopologues being considered `NISTPMX`, the maximum number of electronic states `NSTATEMX`, the maximum number of fitting parameters `NPARMX`, the maximum number of data `NDATAMX`, as well as the maximum order l allowed in the Dunham expansions of Eq. (2) or NDE polynomial expansion parameters of Eqs. (10) and (11) `NDUNMX`, and the maximum number of observed vibrational levels in any of the electronic states considered `NVIBMX`. A user should edit file `arrsizes.h` and give these parameters values appropriate for the types of systems they will be considering before compiling the code.

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 which 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 Section IV.

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 TEX or 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. Finally, the channel–10 output file contains the correlation matrix associated with the fit.

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:

```
# UNIX shell  rdpar  to execute the compiled version of program DParFit named
#   dpar.x, which is stored in the directory /userpath/.  The channel-5 input
#   data file  $1.5  and the output files  $1.6, $1.7, etc. are all in the same
#   (not necessarily current) directory, while the name and location of the
#   file containing the experimental data is read in the channel-5 data file.
#
if [ -e fort.7 ]; then
  rm fort.7
  fi
if [ -e fort.8 ]; then
  rm fort.8
  fi
if [ -e fort.9 ]; then
  rm fort.9
  fi
if [ -e fort.10 ]; then
  rm fort.10
  fi
time /userpath/dpar.x  < $1.5 > $1.6
if [ -e fort.7 ]; then
  mv fort.7 $1.7
  fi
if [ -e fort.8 ]; then
  mv fort.8 $1.8
  fi
if [ -e fort.9 ]; then
  mv fort.9 $1.9
  fi
if [ -e fort.10 ]; then
  mv fort.10 $1.10
  fi
if [ -e MAKEPRED ]; then
  rm MAKEPRED
  fi
```

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.) Use of this shell will cause the standard output from channel–6 to be written to file `filename.6` and the channel–7, channel–8 ... etc. output to files `filename.7`, `filename.8`, ... etc., all of which are located in the same directory as the `filename.5` channel–5 input data file. This grouping of all output for a give case in a family of files with related filenames greatly facilitates book-keeping when performing fits for a range of different cases.

C. Generating Sets of Predicted Transition Energies

A capability introduced in recent versions (V. 3.2 and later) of DParFit 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 $^{\#}40$ in the channel–5 instruction data file to read specifications and selection rules for bands for which the user wishes to generate predictions, and the resulting predictions are written to file `filename.8`.

IV. DATA FILE STRUCTURE AND INPUT PARAMETER DEFINITIONS

A. The Experimental-Data Input File

The experimental data are read from a file whose name is specified in the regular channel–5 input data file (see READ $^{\#}2$). The data must be collected into separate vibrational bands (or fluorescence series, or sets of photo-association spectroscopy (PAS) binding energies, or groups of B_v values), each characterized by the upper and lower vibrational quantum numbers $v' = \text{VP}$ and $v'' = \text{VPP}$, respectively, by the two-alphameric-character labels `LABLP` and `LABLPP` (enclosed between single quotes; e.g. $'\text{X0}'$) chosen to represent the upper and lower electronic states, and by the mass numbers `MN1` and `MN2` of the atoms forming that particular isotopologue. The electronic state labels must correspond to the names used to identify the different electronic states in the channel–5 input (see below).

For each such band, the data are read, one per line, each datum consisting of the upper and lower rotational quantum numbers, $J' = \text{JP}$ and $J'' = \text{JPP}$, respectively, the integer $+1$ (for e–parity levels) or -1 (for f–parity levels) defining the e/f parity of the upper ($p' = \text{EFP}$) and lower ($p'' = \text{EFPP}$) level, the experimental datum $y_{\text{obs}}(i) = \text{FREQ(i)}$ and its uncertainty $u(i) = \text{UFREQ(i)}$. A datum line with $\text{JP} < 0$ signals the end of the data for this band and asks the program to start the input for a new band. The overall data input is assumed to be complete either at the end of the data file or when a negative value of the band-label quantum number $v' = \text{VP}$ is encountered.

```
      IBAND= 0
      COUNT= 1
   10 IBAND= IBAND+ 1
#1    READ(4,*,END=20)  VP(IBAND), VPP(IBAND), LABLP, LABLPP, MN1, MN2
      IF(VP(IBAND.LT.0) GOTO 20
#2  5 READ(4,*)  JP(COUNT), EFP(COUNT), JPP(COUNT), EFPP(COUNT),
    1            FREQ(COUNT), UFREQ(COUNT)
      IF(JP(COUNT).GE.0) THEN
         COUNT= COUNT+1
         GOTO 5
       ELSE
         COUNT= COUNT-1
         GOTO 10
       ENDIF
   20 CONTINUE
```

For a fluorescence series, this band-type data structure is retained, but the definitions of the 'band' and individual datum labels differ. In particular, setting the input parameter $\mathtt{LABLP} = \mathtt{'FS'}$ identifies the data group as a fluorescence series and causes the 'band' parameters $\mathtt{VP}$ and $\mathtt{VPP}$ (see READ [#]1 above) to be defined as the emitting level vibration-rotation quantum numbers v' and J', respectively, and the transition labels $\mathtt{JP}$ and $\mathtt{JPP}$ (READ [#]2 above) as the final (lower) state vibration-rotation quantum numbers v'' and J'', respectively. The parity label parameters $\mathtt{EFP}$ and $\mathtt{EFPP}$ retain their usual significance, and by definition the former has the same value for all lines in a given fluorescence series 'band' or data-group. Note that for a fluorescence series the quantities v', J' and $\mathtt{EFP}$ are merely used to label the various series, and they have no physical significance as far as the analysis is concerned. Moreover, program operation is not affected if the same values of these quantities are used for several different series; it just means that the different fitted origins for those several fluorescence series will have the same label in the printed output file.

Another distinct data type which can be input using this same band-type data structure is a set of individual-level binding energies, such as those yielded by photo-association spectroscopy (PAS). In this case the nature of this data-group is identified by making the input upper-electronic-state band label $\mathtt{LABLP} = \mathtt{'PA'}$. As with fluorescence series, the data parameters $\mathtt{JP}$, $\mathtt{JPP}$ and $\mathtt{EFPP}$ are defined as the final-state level parameters v'', J'' and parity p'', respectively, while the 'band parameters' $\mathtt{VP}$ and $\mathtt{VPP}$ and the data parameter $\mathtt{EFP}$ are all dummy variables which are ignored by the analysis.

The defining property of $\mathtt{PA}$-type data is that they are (positive number) binding energies relative to the dissociation asymptote of the given electronic state. They have special significance in the data analysis only if the vibrational energies are represented by an expression in which the dissociation limit is an explicit parameter, i.e., only if pure-NDE or MXS functions are used for the vibrational energies. If this is not the case, DParFit simply treats a $\mathtt{PA}$-type data-group as an ordinary fluorescence series.

A final additional type of input data which the program can accept and include in a fit is a set of experimentally determined B_v values for a given electronic state. While unusual, the inclusion of indirectly-obtained data of this type is sometimes necessary when the available measurements are fragmentary or incomplete (e.g., see Ref. 62). As for fluorescence-series or PAS data, the band-type data structure is retained, but in this case the input parameter value $\mathtt{LABLP} = \mathtt{'BV'}$ identifies this data-group as a set of B_v values for electronic state $\mathtt{LABLPP}$, and signals that the band parameters $\mathtt{VP}$ & $\mathtt{VPP}$ and the transition labels $\mathtt{JPP}$, $\mathtt{EFP}$ & $\mathtt{EFPP}$ are dummy variables, while input parameter $\mathtt{JP}$ is actually the vibrational quantum number v, $\mathtt{FREQ}$ is the B_v value and $\mathtt{UFREQ}$ its uncertainty.

As an illustration of this data file structure, the listing below presents fragments of an experimental data file used for an analysis of the chemiluminescence spectrum of $^{138}\mathrm{BaO}$, $^{137}\mathrm{BaO}$, $^{136}\mathrm{BaO}$, $^{135}\mathrm{BaO}$. In addition to the new electronic chemiluminescence spectra reported in that work,[52] the analysis used MW and IR data and two older OODR fluorescence series taken from the literature. Although the OODR data had uncertainties two orders of magnitude larger than the chemiluminescence data (0.5 $vs.$ 0.005 cm^{-1}), they were included because of their much greater vibrational range ($v''=0-34$ $vs.$ $0-20$). Note that text beginning at the "$\%$" sign on a line of input data file are comments which are ignored by the program.

```
 7 7  'A0' 'A0'    137 16            %  v' v"  LABLP LABLPP  MN1 MN2
2 1  1 1  0.998277282  0.000050035   %  J' p' J" p" FREQ UFREQ
-1 1  -1 1  -1.1  -1.1               %  Microwave data from the literature
 7 7  'A0' 'A0'    137  16           %   incorporated into our analysis
3 1  2 1  1.497415922  0.000050035
-1 1 -1 1  -1.1  -1.1


 3 2  'X0' 'X0'    137 16            %  v' v"  LABLP LABLPP  MN1 MN2
 7 1   6 1  661.99806  0.01          %  J' p' J" p" FREQ UFREQ
25 1  24 1  672.27464  0.01          %  Infrared data from the literature
39 1  38 1  679.59709  0.01          %    incorporated into our analysis.
14 1  15 1  648.17157  0.01
19 1  20 1  644.84254  0.01
24 1  25 1  641.44710  0.01
-1 1  -1 1  -1.1  -1.1
```

```
  0 6  'A0' 'X0'   135 16              %  v' v"  LABLP LABLPP  MN1 MN2
 47 1  48 1  12653.22414  0.005        %  J' p' J" p" FREQ UFREQ
 43 1  44 1  12672.26623  0.005        %  A vibrational band from the new
 35 1  36 1  12705.94541  0.005        %    chemiluminescence spectrum.
 33 1  34 1  12713.45841  0.005
 32 1  33 1  12717.06675  0.005
 30 1  31 1  12724.03656  0.005
 28 1  29 1  12730.63128  0.005
 25 1  26 1  12739.85293  0.005
 24 1  25 1  12742.74558  0.005
 20 1  21 1  12753.38391  0.005
 19 1  20 1  12755.81818  0.005
 13 1  14 1  12768.52559  0.005
  7 1   8 1  12777.95445  0.005
 -1 1  -1 1   -1.0   -1.0

 15  50  'FS' 'X0'    138  16          %  v' J'  LABLP LABLPP  MN1 MN2
  0  1  49  1  37678.6  5.0            %  v" p' J" p" FREQ UFREQ
  1  1  49  1  37018.0  1.7            %  OODR fluorescence series R lines
  2  1  49  1  36359.8  1.7            %    from Field [JCP 63,3228 (1975).
  3  1  49  1  35706.8  1.7
.... omit 25 intermediate lines ...
 32  1  49  1  18705.0  2.3
 33  1  49  1  18194.3  1.5
 34  1  49  1  17688.2  1.2
 -1  1  -1  1  -1.1  -1.1
```

B. The Channel–5 Input File: Defining the Problem and Specifying the Fit

The logical structure and read statements governing the channel–5 data input describing the system to be treated, specifying the type of fit to be carried out, and inputting any necessary system parameters, is shown below. The following subsection then provides a detailed description of the nature of and/or options associated with each of the input variables. In most cases only a very small fraction if these read statements are actually used.

```
#1   READ(5,*)  AN(1), AN(2), CHARGE, NISTP, NSTATES
#2   READ(5,*)  DATAFILE
#3   READ(5,*)  UCUTOFF, IROUND, ROBUST, LPRINT, PRINP
     DO  ISOT= 1, NISTP
#4      READ(5,*) MN(1,ISOT), MN(2,ISOT)
        ENDDO
  c***********************************************************************
  c     Begin loop over electronic states
  c***********************************************************************
     DO 60 ISTATE= 1, NSTATES
#5      READ(5,*) SLABL(ISTATE), IOMEG(ISTATE), JTRUNC(ISTATE), EFSEL(ISTATE),
   1                                            VMIN(ISTATE), VMAX(ISTATE)
#6      READ(5,*) NCDC(ISTATE), NDEGv(ISTATE), NDEBv(ISTATE), NDECDC(ISTATE),
   1            IFXGv(ISTATE), IFXBv(ISTATE), IFXCDC(ISTATE), BOBORD(ISTATE)
        MMAX= NCDC(ISTATE)+ 1
        IF(NDEGv(ISTATE).EQ.-1) THEN
            DO  ISOT= 1,NISTP
               DO  I= VMIN(ISTATE), VMAX(ISTATE)
               IF(IFXGv.GT.0) THEN
#7                  READ(5,*) IV, (ZK(M,IV,ISTATE,ISOT), M= 0,MMAX)
                 ELSE
#8                  READ(5,*,END=200) IV, FITGV(IV,ISTATE,ISOT), NRC(IV,ISTATE,ISOT)
                ENDO
             ENDO
           IF(IOMEG(ISTATE).NE.0) GO TO 30
           GO TO 60
           ENDIF
#9      IF(NDEGv(ISTATE).EQ.2) READ(5,*) VS(ISTATE), DVS(ISTATE), IFXVS(ISTATE),
```

19

```fortran
    1                                                                    IFXDVS(ISTATE)
          IF((NDEGv(ISTATE).EQ.0).OR.(NDEGv(ISTATE).GE.2)) THEN
#10           READ(5,*) LMAX(0,ISTATE)
              IF(IFXGv(ISTATE).GT.0) THEN
#11               READ(5,*) Te(ISTATE)
#12               READ(5,*) (YLM(L,0,ISTATE), L= 1, LMAX(0,ISTATE))
                  ENDIF
              ENDIF
          IF(NDEGv(ISTATE).GE.1) THEN
#13           READ(5,*) NLR(ISTATE), DLIMIT(ISTATE), vD(ISTATE), Cn(ISTATE), NSIG
#14           READ(5,*) ITYPE(ISTATE), NP0(ISTATE), NQ0(ISTATE), IP0(ISTATE), IQ0(ISTATE)
#15           IF(NP0(ISTATE).GT.0) READ(5,*) (PM0(I,ISTATE),I=1, NP0(ISTATE))
#16           IF(NQ0(ISTATE).GT.0) READ(5,*) (QM0(I,ISTATE),I=1, NQ0(ISTATE))
#17           IF(IFXGv(ISTATE).LE.0) READ(5,*) IFXD(ISTATE), IFXvD(ISTATE)
              ENDIF
          IF((NDEBv(ISTATE).EQ.-1).AND.(NDEGv(ISTATE).GE.0)) THEN
              DO  ISOT= 1,NISTP
                  DO  I= VMIN(ISTATE), VMAX(ISTATE)
                      IF(IFXBv.GT.0) THEN
#18                       READ(5,*) IV, (ZK(M,I,ISTATE,ISOT), M= 1,MMAX)
                        ELSE
#19                       READ(5,*,END=200) IV, NRC(IV,ISTATE,ISOT)
                      ENDO
                  ENDO
              GO TO 30
              ENDIF
          IF((NDEBv(ISTATE).EQ.0).OR.(NDEBv(ISTATE).EQ.2)) THEN
#20           READ(5,*) LMAX(1,ISTATE)
#21           IF(IFXBv(ISTATE).GT.0) READ(5,*) (YLM(L,1,ISTATE), L= 0, LMAX(1,ISTATE))
              ENDIF
          IF(NDEBv(ISTATE).GE.1) THEN
#22           READ(5,*) ITYPB(ISTATE), NP1(ISTATE), NQ1(ISTATE),
     1                                         IP1(ISTATE), IQ1(ISTATE)
#23           IF(NP1(ISTATE).GT.0) READ(5,*) (PM1(I,ISTATE), I=1,
     1                                                  NP1(ISTATE))
#24           IF(NQ1(ISTATE).GT.0) READ(5,*) (QM1(I,ISTATE), I=1,
     1                                                  NQ1(ISTATE))
              ENDIF
          IF(NDECDC(ISTATE).EQ.-1).and.(IFXCDC(ISTATE).GT.0).and.((NDEBv(ISTATE).GE.0).or.(IFXBv(ISTATE).LE
              DO  ISOT= 1,NISTP
                  DO  I= VMIN(ISTATE), VMAX(ISTATE)
#25                   READ(5,*) IV, (ZK(M,IV,ISTATE,ISOT), M= 2,MMAX)
                      ENDDO
                  ENDDO
              ENDIF
          IF((NDECDC(ISTATE).EQ.-1).AND.(IFXCDC(ISTATE).LE.0)) THEN
              DO  ISOT= 1,NISTP
                  DO  IV= VMIN(ISTATE),VMAX(ISTATE)
#26                   READ(5,*,END=200) IV, NRC(IV,ISTATE,ISOT)
                      ENDDO
                  ENDDO
              ENDIF
          IF(NDECDC(ISTATE).EQ.0) THEN
#27           READ(5,*) (LMAX(M,ISTATE),M= 2, NCDC(ISTATE)+1)
              IF(IFXCDC(ISTATE).GT.0) THEN
                  DO  M= 2, NCDC(ISTATE)+1
#28                   READ(5,*) (YLM(L,M,ISTATE),L= 0, LMAX(M,ISTATE))
                      ENDDO
                  ENDIF
          IF(NDECDC(ISTATE).GE.1) THEN

                                        20
```

```fortran
                MMAX= NCDC(ISTATE)+ 1
#29             READ(5,*) (LMAX(M,ISTATE),M= 2, MMAX)
                DO  M= 2,MMAX
#30                 READ(5,*)  (RM(I),I= 1, LMAX(M,ISTATE))
                    ENDDO
                ENDIF
        30 IF(IOMEG(ISTATE).NE.0) THEN
#31             READ(5,*) NLDMX(ISTATE), efREF(ISTATE), NDELD(ISTATE), IFXLD(ISTATE)
                MQ0= MAX0(0,IOMEG(ISTATE)-1)
                IF(NLDMX(ISTATE).GT.0) THEN
                    IF(NDELD(ISTATE).EQ.-1) THEN
                        DO  ISOT= 1, NISTP
                            DO  IV= VMIN(ISTATE), VMAX(ISTATE)
#32                             IF(IFXLD(ISTATE).GT.0) READ(5,*) IV,
      1                                 (ZQ(MQ0+M,IV,ISTATE,ISOT), M= 1,NLDMX(ISTATE))
#33                             IF(IFXLD(ISTATE).LE.0) READ(5,*) IV, NQC(IV,ISTATE,ISOT)
                                ENDDO
                            ENDDO
                        ENDIF
                    IF(NDELD(ISTATE).GE.0) THEN
#34                     READ(5,*) (LDMAX(MQ0+M,ISTATE),M= 1,NLDMX(ISTATE))
                        IF(IFXBv(ISTATE).GT.0) THEN
                            DO  M= 1, NLDMX(ISTATE)
#35                             IF(LDMAX(M,ISTATE).GE.0) READ(5,*) (QLM(L,M,ISTATE),
      1                                                        L=0, LDMAX(M,ISTATE))
                                ENDDO
                            ENDIF
                        ENDIF
                    ENDIF
                ENDIF
            IF(BOBORD(ISTATE).GE.0) THEN
#36             IF((IFXGv(ISTATE).LE.0).AND.(ISTATE.EQ.1)) READ(5,*) BOB00
#37             READ(5,*) (LAMAX(1,M,ISTATE), M= 0, BOBORD(ISTATE))
#38             IF(AN(1).NE.AN(2)) READ(5,*) (LAMAX(2,M,ISTATE), M= 0, BOBORD(ISTATE))
                IF(IFXGv(ISTATE).GT.0) THEN
                    ATOM2= 2
                    IF(AN(1).EQ.AN(2)) ATOM2= 1
                    DO  ATOM= 1,ATOM2
                        DO  M= 0, BOBORD(ISTATE)
                            IF(LAMAX(ATOM,M,ISTATE).GE.0) THEN
#39                             READ(5,*) (DELTA(ATOM,L,M,ISTATE), L=0, LAMAX(ATOM,M,ISTATE))
                                ENDIF
                            ENDDO
                        ENDDO
                    ENDIF
                ENDIF
        60 ENDDO
  c************************************************************************
  c        End of loop over electronic states and of Channel-5 input
  c************************************************************************
      IF(DATAFILE.EQ.MAKEPRED) THEN
  77      CONTINUE
#40       READ(5,*) VP(IBAND),VPP(IBAND),LABLP,LABLPP,MN1,MN2,PP,PPP,
      1                                            JMAXX,J2DL,J2DU,J2DD
          IBAND= IBAND+ 1
          IF(VP(IBAND).GE.0) GO TO 77
          ENDIF
  c************************************************************************
  c        End of Channel-5 input data file
  c************************************************************************
```

C. Definitions and Descriptions for the Channel-5 Input File Data

Read integers identifying the molecule and some features of the system.

$^{\#}$1. READ(5,*) AN(1), AN(2), CHARGE, NISTP, NSTATES

> AN(1) & AN(2): integer atomic numbers of the atoms 1 & 2 forming the molecule.
>
> CHARGE: ($\pm$) integer for the total charge on the molecule. It is used to generate the charge-modified reduce mass used for molecular ions,[46] $\mu = M_A M_B/(M_A + M_B - m_e \times \text{CHARGE})$, where m_e is the electron mass.
>
> NISTP: the number of distinct isotopologues to be considered in this analysis.
>
> NSTATES: the number of different electronic states considered in this analysis.

Read the name of the file containing the experimental data to be fitted in the analysis.

$^{\#}$2. READ(5,*) DATAFILE

> DATAFILE: is the name for the file containing the experimental data to be fitted; it may consist of up to 30 alphanumeric characters and must be enclosed in single quotes with no leading blanks (e.g., 'Li2B(A-X).4'). If the file does not reside in the current directory, this name must include the absolute or relative path. Note that if this file contains data for more states and/or isotopologues than those considered in this particular analysis, they are simply ignored, so it is not necessary to construct a separate data file if one wishes to consider only a subset of the data (e.g., only the microwave transitions, or only data for one isotopologue).
> • If the program is being asked to predict data from a set of known input parameters (see § III.C), the filename read here *must* be MAKEPRED (i.e., the data file entry must be 'MAKEPRED').

Read parameters to set global restrictions on the data to be used (without editing the experimental data file), and to specify general features of the fit and output.

$^{\#}$3 READ(5,*) UCUTOFF, IROUND, ROBUST, LPRINT, PRINP

> UCUTOFF: neglect any input data with uncertainties $u(i) > \text{UCUTOFF}$ (a real number).
>
> IROUND: Setting (integer) $\text{IROUND} \neq 0$ causes the "sequential rounding and refitting" procedure of Ref. 60 to be implemented, with each parameter being rounded at the $|\text{IROUND}|$'th significant digit of its uncertainty. If $\text{IROUND} > 0$ the sequential rounding is applied in turn to the remaining free parameter with the largest relative uncertainty; if $\text{IROUND} < 0$ the rounding proceeds sequentially from the last parameter to the first. If $\text{IROUND} = 0$ the fit simply stops after full convergence and performs no parameter rounding; this last option saves considerable computation time, and would normally be chosen except for a "final" fit to obtain parameters for publication and/or distribution.
>
> ROBUST: is an integer which is set > 0 to cause the *robust* fitting procedure described at the end of § III.A to be applied; otherwise (the normal case) set it ≤ 0.
>
> LPRINT: an integer specifying the level of output to be generated by the least-squares subroutine package NLLSSRR. Setting it $= 0$ yields no internal printout except for convergence-failure warning messages; this is the recommended choice when there are no problems with the fits. If $\text{LPRINT} < 0$ print converged unrounded parameters; if $\text{LPRINT} \geq 1$ also print converged rounded parameters (when $\text{IROUND} \neq 0$); if $\text{LPRINT} \geq 2$ also print parameter changes on each rounding step; if $\text{LPRINT} \geq 3$ also report parameter convergence criterion satisfied; if $\text{LPRINT} \geq 4$ also print convergence test on each fitting cycle; if $\text{LPRINT} \geq 5$ also print parameter changes & uncertainties on each fitting cycle.

PRINP: is an integer parameter which controls whether (PRINP > 0) or not (≤ 0) a summary of the experimental data is printed immediately after it is input. This option is useful only for helping locate problems in the input data; in most cases one should set PRINP = 0 .

Loop over the NISTP isotopologues, and for each, read the integer mass numbers of the two atoms. The first isotopologue is defined as the reference species (ISOT = α = 1) for parameter mass-scaling and the calculation of BOB corrections. The mass numbers for each isotopologue must be on a different line.

#4 READ(5,*) MN(1,ISOT), MN(2,ISOT)

   MN(1,ISOT) & MN(2,ISOT): integer mass numbers of the atoms/particles 1 & 2 forming the iso-
   topologue α = ISOT. For a normal stable atomic isotope, its mass is taken from the tabulation
   in subroutine MASSES; if MN is outside the range for the normal stable isotopes of that atom,
   the abundance-averaged atomic mass is used.

Now begin the loop over the NSTATES electronic states to be considered in the analysis. This loop from $s \equiv$ ISTATE = 1 to NSTATES includes almost all of the rest of the channel–5 input.

First, read parameters characterizing the state, and (if desired) setting limits on the range of the rotational and vibrational levels to be considered for it.

#5. READ(5,*) SLABL(s), IOMEG(s), JTRUNC(s), EFSEL(s), VMIN(s), VMAX(s)

   SLABL: a two-alphanumeric-character label for this electronic state, inclosed in single quotes (e.g.,
   ′X0′, ′a1′, ′f+′, ...), to identify it in the output and in the experimental data input file.

   IOMEG: If IOMEG ≥ 0 the electronic state is treated as a spin singlet with integer electronic angular
   momentum projection quantum number IOMEG. For a state with $^2\Sigma$ symmetry, set IOMEG = −2.

   JTRUNC: an integer data-selection parameter. If JTRUNC > 0 , omit from the analysis all data for
   this electronic state with $J >$ JTRUNC; if JTRUNC < 0 omit all data with $J <$ JTRUNC.

   EFSEL: an integer which allows a user to consider: a) only transitions involving e–parity levels
   of this state if EFSEL > 0 , b) only transitions involving f–parity levels if EFSEL < 0 , c) all
   transitions if EFSEL = 0 .

   VMIN & VMAX: data-range selection parameters. Omit from the analysis all data for this state
   associated with vibrational levels outside the range VMIN to VMAX.

Read integers specifying the type of representation to be used for the vibrational and rotational parameters, and which ones are to be held fixed or set free.

#6 READ(5,*) NCDC(s), NDEGv(s), NDEBv(s), NDECDC(s), IFXGv(s), IFXBv(s), IFXCDC(s),
              BOBORD(s)

   NCDC: the number of CDC s to be considered in fits to Dunham, NDE or MXS functions for this
   state. It is a dummy parameter if band constants or individual term values are used.

   NDEGv: specifies whether G_v for this state is to be represented: a) by the individual band constants
   $\{K_m^{(\alpha)}(v)\} = \{G_v^{(\alpha)}, B_v^{(\alpha)},$ etc.$\}$ of Eq. (1) for NDEGv = −1 (this case also requires that NDEBv =
   NDECDC = −1), b) by the Dunham expansion of Eq. (4) for NDEGv = 0 , c) by the pure NDE
   expressions of Eqs. (7) - (11) for NDEGv = 1 , or d) by the Tellinghuisen-type MXS "mixed"
   representation of Eq. (13) for NDEGv = 2 . If levels of this state are to be represented by
   independent term values $\{T^{(\alpha)}(v, J, p)\}$, set NDEGv = −2 .

   NDEBv: as for NDEGv, specifies whether B_v for this state is to be represented: a) by the individual
   band constants of Eq. (1) if NDEBv = −1 (this case also requires that NDECDC = −1); b) by the
   Dunham expansion of Eq. (5) if NDEBv = 0 , c) by the pure NDE expressions of Eqs. (8) - (11)
   if when NDEBv = 1 (only allowed if NDEGv ≥ 1), or d) by the Tellinghuisen-type MXS "mixed"
   representations of Eq. (14) if NDEBv = 2 (this option is only allowed if also NDEGv = 2).

NDECDC : as for NDEGv and NDEBv, specifies whether the CDCs for this state are to be represented: a) by the individual band constants $\{K_m^{(\alpha)}(v)\} = \{-D_v^{(\alpha)}, H_v^{(\alpha)}, ...\}$ of Eq. (1) for NDECDC $= -1$ [*Note* that if G_v or B_v are represented by band constants (NDEGv or NDEBv $= -1$), necessarily NDECDC $= -1$.], b) by the Dunham expansions of Eq. (15) for NDECDC $= 0$, or c) by the NDE expressions of Eqs. (8), (9) & (11) for NDECDC $= 1$; this last case requires IFXCDC $= 1$.

IFXGv , IFXBv & IFXCDC : are integers set > 0 if G_v, B_v or the CDCs, respectively, are to be held fixed at values determined by read-in parameters; otherwise (if ≤ 0) determine them from the fit. *Note* that if G_v is represented by band constants (NDEGv $= -1$), the program requires that IFXBv $=$ IFXGv $=$ IFXCDC.

BOBORD : indicates whether or not atomic-mass-dependent Born-Oppenheimer breakdown (BOB) correction terms are to be considered for this state. If BOBORD ≥ 0 consider BOB terms of rotational order (in $[J(J + 1)]$) up to $m =$ BOBORD. These coefficients are fitted or held fixed, as specified by parameter IFXGv. Setting BOBORD < 0 causes BOB corrections to be omitted.

Representation for the vibrational energies G_v

READ statements ($^\#7 - 17$) are concerned with the four possible ways of representing G_v for electronic state–s: $^\#7 - 8$ govern cases in which band constants are used (NDEGv $= -1$), $^\#9$ is for MXS functions, $^\#10 - 12$ are for Dunham or MXS functions, and $^\#13 - 17$ for NDE or MXS functions.

If band constants are used *and* held fixed (IFXGv > 0), read in their values, looping over the isotopologues $\alpha =$ ISOT, and for each isotopologue looping over the specified range of vibrational levels $v =$ IV $=$ VMIN(s) to VMAX(s), and for each vibrational level read band constants ZK$(m, v, s, \alpha) = K_m^{(\alpha)}(v)$ from Eq. (1), of rotational order (in powers of $[J(J + 1) - \Lambda^2]$) for $m = 0$ to $m =$ MMAX $=$ NCDC$(s) + 1$.

$^\#7$. READ(5,*) IV, (ZK(M,IV,s,ISOT), M=0, MMAX)

If band constants are used for G_v (and hence also for B_v and the CDCs) *and* are to be determined by the fit (IFXGv ≤ 0), loop over the isotopologues ISOT, and for each isotopologue loop over the specified range of vibrational levels $v =$ IV $=$ VMIN(s) to VMAX(s), and for each vibrational level read in constants specifying whether or not this vibrational level defines the reference energy for a 'connected set', and the rotational order (in powers of $[J(J + 1) - \Lambda^2]$) of the level energy expression to be fitted.

$^\#8$. READ(5,*,END=200) IV, FITGV(IV,s,ISOT), NRC(IV,s,ISOT)

IV : is the vibrational index v for this level.

FITGV : is set $= 0$ for the lowest vibrational level of each "connected set", which is given a fixed reference energy of 0; otherwise FITGV > 0 and G_v for this level is determined from the fit.

NRC : is the number of rotational constants $\{K_m^{(\alpha)}(v)\} = \{B_v^{(\alpha)}, -D_v^{(\alpha)}, H_v^{(\alpha)}, ...$ etc.$\}$, to be fitted for level $v =$ IV.

If MXS mixed representation are to be used for G_v (NDEGv ≥ 2), read in *real number* values of $v_s =$ VS(s), the value of v for the switch-over vibrational level, and of $\delta v_s =$ DVS(s), the width parameter for the switching function of Eq. (12) for isotopologue $\alpha = 1$, and integers IFXVS & IFXDVS specifying whether they are to be held fixed (value > 0) or varied (value ≤ 0) in the fit. Note that because of the sensitivity of the fit to their values, VS & DVS should be read in floating point "D" format (e.g., 35.0D0).

$^\#9$. READ(5,*) VS(s), DVS(s), IFXVS(s), IFXDVS(s)

If Dunham or MXS expansions are used for G_v (NDEGv $= 0$ or 2), read in the order of the G_v vibrational polynomial, LMAX(0,s)

$^\#10$. READ(5,*) LMAX(0,s)

If Dunham or MXS expansions are used for G_v (NDEGv$=0$ or 2), and are held fixed (IFXGv>0), read in the reference energy Te$(s)\equiv T^{(\alpha=1)}_{-1/2}$ for this state and the values of the $\{Y^{(\alpha)}_{l,0}\}$ coefficients for the reference isotopologue ISOT$=\alpha=1$. Note that this G_v expansion starts with the linear term.

$^\#11.$ READ(5,*) Te(s)

$^\#12.$ READ(5,*) (YLM(L,0,s), L= 1,LMAX(0,s))

If NDE or MXS functions are used for G_v (NDEGv≥ 1), read in parameters characterizing the particular expansions to be used. If IFXGv≤ 0 the parameters read via statements $^\#16$ & 17 are initial trial values to be optimized by the fit.

$^\#13.$ READ(5,*) NLR(s), DLIMIT(s), vD(s), Cn(s), NSIG

> NLR: is the integer power of the asymptotically-dominant inverse-power term in the long-range potential of Eq. (6), for electronic state–s.
>
> DLIMIT: is the absolute energy $\mathfrak{D}$ at the asymptote of state–s, expressed relative to the reference energy $T^{(1)}_{-1/2} = G(v = -1/2)$ for the first electronic state considered, $s=1$.
>
> vD: is the non-integer effective vibrational index at dissociation, $v_{\mathfrak{D}}$, for isotopologue–1.
>
> Cn: is the coefficient C_n of the long-range potential of Eq. (6).
>
> NSIG: is the number of significant digits in C_n to be retained on calculating a rounded-off value of the limiting near-dissociation theory coefficients $X_m(n, C_n)$ of Eq. (9). Set NSIG ≤ 0 to use C_n precisely as read, with no rounding of the coefficient $X_m(n, C_n)$; this option is not recommended, as it makes the resulting expressions less convenient to work with.

In the NDE expressions for G_v, set ITYPE$=1$ when the vibrational energy expression of Eq. (7) represents $\mathcal{F}^{(\alpha)}_0$ using Eq. (10) with $\mathcal{S} = 1$; ITYPE $= 2$ when $\mathcal{S} = 2n/(n-2)$, and ITYPE$= 3$ when Eq. (11) (with $m=0$) is used for $\mathcal{F}^{(\alpha)}_0$ in Eq. (7).

- For ITYPE$=1$ or 2, NP0$=L+1-t$ and NQ0$=M+1-t$ are the numbers of coefficients, PMO$(i)=p^{(1),0}_i$ and QMO$(j)=q^{(1),0}_j$, respectively, in the numerator and denominator expansions of Eq. (10).
- For ITYPE$=3$, NP0 is the numbers of coefficients PMO$(i)=p^{(1),0}_i$ in the exponent expansion of Eq. (11) (starting from $i = t$).
- IP0$=$IQ0$=t$ is the leading power in the numerator and denominator expansions of Eqs. (10) & (11).
- *Note that* if either of NP0 or NQ0 are ≤ 0, the READ statement for the associated parameters (PMO or QMO) is omitted. Necessarily IP0$=$IQ0$=t \geq 1$.

$^\#14.$ READ(5,*) ITYPE(s), NP0(s), NQ0(s), IP0(s), IQ0(s)

$^\#15.$ READ(5,*) (PMO(I,s), I=1, NP0(s))

$^\#16.$ READ(5,*) (QMO(I,s), I=1, NQ0(s))

If an NDE or MXS expression for G_v is being fitted (IFXGv≤ 0), one must now read integers specifying whether the parameters DLIMIT$(s)=\mathfrak{D}$ and vD$(s)=v_{\mathfrak{D}}(s)$ are to be held fixed (when IFXD and/or IFXvD, respectively, are >0), or to be optimized by the the fit (when IFXD and/or IFXvD, respectively, are ≤ 0). Skip this READ statement if IFXGv>0.

$^\#17.$ READ(5,*) IFXD(s), IFXvD(s)

Representation for the inertial rotational constants B_v

Use READ statements $^\#18 - 19$ if band constants are to be used for B_v, but *not* for G_v; this case requires the CDCs to also be represented by band constants.

- If rotational band constants are to be held fixed, read in their values, looping first over isotopologues $\alpha=$ ISOT, and for each isotopologue loop over the specified range of vibrational levels $v=$ IV$=$ VMIN(s) to

`VMAX(`s`)`, and for each vibrational level read rotational constants `ZK(`m`,` v`,` s`,` α`)`$=K_m^{(\alpha)}(v)$ (see Eq. (1)) of order $m=1$ to `NCDC(`s`)` $+1$.

$^{\#}$18. `READ(5,*) IV, (ZK(M,IV,`s`,ISOT), M=1,NCDC(`s`)+1)`

• If rotational band constants are to be fitted (while `NDEGv` ≥ 0), loop over the isotopologues $\alpha=$ `ISOT`, and for each isotopologue loop over the specified range of vibrational levels $v=$ `IV` $=$ `VMIN(`s`)` to `VMAX(`s`)`, and for each vibrational level read in constants specifying the order (e.g., in powers of $[J(J+1)-\Lambda^2]$) of the rotational expansion (including CDCs) to be used.

$^{\#}$19. `READ(5,*,END=200) IV, NRC(IV,`s`,ISOT)`

If a Dunham or MXS expansion is used for B_v (`NDEBv` $=0$ or 2), read in the order `LMAX(1,`s`)` of the B_v vibrational polynomial.

$^{\#}$20. `READ(5,*) LMAX(1,`s`)`

If using a Dunham or MXS representation for B_v and values are to be held fixed (`IFXBv` >0), read in the values of the coefficients $\{Y_{l,1}^{(\alpha)}\}$ for the reference isotopologue `ISOT` $=\alpha=1$.

$^{\#}$21. `READ(5,*) (YLM(L,1,`s`), L= 0, LMAX(1,`s`))`

If an NDE function from Eq. (8), (9) and (11) is used for B_v (`NDEBv` >0), read the parameters defining the type of NDE expansion and the initial trial values of the expansion parameters. The function types and parameter definitions are precisely analogous to the vibrational case: see description of READ $^{\#}$14-16.

$^{\#}$22. `READ(5,*) ITYPE(`s`), NP1(`s`), NQ1(`s`), IP1(`s`), IQ1(`s`)`

$^{\#}$23. `READ(5,*) (PM1(I,`s`), I=1, NP1(`s`))`

$^{\#}$24. `READ(5,*) (QM1(I,`s`), I=1, NQ1(`s`))`

Representing the centrifugal distortion constants (CDCs)

READ statements $^{\#}$25−30 specify how the CDCs for electronic state–s are to be represented. Use READs $^{\#}$25 − 26 if band constants are to be used for the CDC's but were *not* used for B_v.

If the CDCs are to be held fixed at values defined by read-in band constants (`NDECDC` $=-1$ and `IFXCDC` >0), and G_v and B_v *are not* fixed in this manner (otherwise, the fixed CDCs would have been input via READ $^{\#}$7 or 18), read those values here, looping over isotopologues $\alpha=$ `ISOT`, and for each isotopologue looping over the range of vibrational levels $v=$ `IV` $=$ `VMIN(`s`)` to `VMAX(`s`)` considered for this state.

$^{\#}$25. `READ(5,*) IV, (ZK(M,I,`s`,ISOT), M= 2,NCDC(`s`)+1)`

• If CDCs are to be fitted as band constants (but B_v's are not), loop over the isotopologues $\alpha=$ `ISOT`, and for each isotopologue loop over the specified range of vibrational levels $v=$ `IV` $=$ `VMIN(`s`)` to `VMAX(`s`)`, and for each vibrational level `IV`, read an integer `NRC` specifying the total order (e.g., in powers of $[J(J+1)-\Lambda^2]$) of the rotational expansion to be used. The number of CDCs to be fitted for that v is `NRC=1`.

$^{\#}$26. `READ(5,*,END=200) IV, NRC(IV,`s`,ISOT)`

If Dunham expansions are used for the CDCs (`NDECDC` $=0$), read the (integer) orders `LMAX(M,`s`)` of the vibrational expansions of Eq. (15), for each of the `NCDC` rotational orders `M`.

$^{\#}$27. `READ(5,*) (LMAX(M,`s`), M= 2, NCDC(`s`)+1)`

If the CDCs are represented by Dunham expansions *and* are held fixed (`IFXCDC` >0), loop over the `NCDC(`s`)` orders m $(=$`M`$)$, reading the fixed Dunham parameters for each. If the read-in value of `LMAX(M,`s`)` <0, the program skips the associated read statement.

$^{\#}$28. `READ(5,*) (YLM(L,M,`s`),L= 0, LMAX(M,`s`))`

If the CDCs are represented using the NDE functions of Eqs. (8), (9) and (11) (only allowed if the CDCs are held fixed, `IFXCDC` >0), read the orders `LMAX(M,`s`)` of the exponent expansions of Eq. (11) for those

CDCs, and then loop over the NCDC(s) orders, and for each one read the associated exponent expansion parameters RM(I) $= p_i^{(\alpha),m}$ for the reference isotopologue $\alpha = 1$. READ #30 is skipped if LMAX(M,s) ≤ 0 for that order M.

#29. READ(5,*) (LMAX(M,s), M= 2, NCDC(s)+1)

#30. READ(5,*) (RM(I), I= 1, LMAX(M,s))

Λ–doubling or $^2\Sigma$ splittings

If IOMEG(s) $\neq 0$ for electronic state–s, read parameters governing how the associated Λ-doubling or $^2\Sigma$ splitting is to be described.

#31. READ(5,*) NLDMX(s), efREF(s), NDELD(s), IFXLD(s)

> NLDMX: specifies the number of rotational terms (i.e., the number of terms in the sum over m in Eqs. (16 – 17) or Eqs. (19 – 22)) in the expression be used for Λ–doubling or $^2\Sigma$ splitting for this state. If NLDMX ≤ 0 ignore such splittings and skip READs #32 − 35.

> efREF: specifies the choice of reference (or zero-shift) parity levels for Λ–doubling splittings for this state as being the f–parity sublevels when efREF $= -1$, the e–parity sublevels when efREF $= +1$, or their mid-point when efREF $= 0$; e.g., for a $^1\Pi$ state, if efREF $= -1$ the f–levels are treated as unperturbed and the e–levels shifted by $+ q_B(v)[J(J+1)]$, etc. This is a dummy parameter for $^2\Sigma$ splitting.

> NDELD: specifies the type of representation to be used for Λ–doubling or $^2\Sigma$ splitting terms. If NDELD $= -1$ use a band-constant form, while if NDELD ≥ 0 use Dunham-type $(v+\frac{1}{2})$ polynomials.

> IFXLD: an integer > 0 if the Λ–doubling or $^2\Sigma$ splitting constants are to be held fixed at values determined by read-in parameters; otherwise (if IFXLD ≤ 0) determine them from the fit.

If NLDMX(s) > 0 and band constant are being used (NDELD(s) $= -1$) and held fixed (IFXLD(s) > 0) for electronic state–s, loop over the isotopologues $\alpha =$ ISOT, and for each isotopologue loop over the specified range of vibrational levels $v =$ IV $=$ VMIN(s) to VMAX(s), and for each vibrational level read the vibrational index $v =$ IV and the Λ–doubling constants ZQ(MQO $+ m$, v, s, α) $= q_m^{(\alpha)}(v)$ for $m = 1$ to NLDMX(s). MQO is defined internally to specify the rotational order of the leading coefficient for this case.

#32. READ(5,*) IV, (ZQ(MQO+M,IV,s,ISOT), M= 1, NLDMX(s))

If NLDMX(s) > 0 and band constant are being used (NDELD(s) $= -1$) and fitted (IFXLD(s) ≤ 0) for electronic state–s, loop over the isotopologues $\alpha =$ ISOT, and for each isotopologue loop over the specified range of vibrational levels $v =$ IV $=$ VMIN(s) to VMAX(s), reading the vibrational index IV and an integer NQC(v,s,α) specifying the number of rotational terms in the sum over m in Eq. (16), (19) or (21), to be determined for that particular vibrational level. Set NQC ≤ 0 if IOMEG(s) $= 0$ or if one has no distinct e/f data to allow determination of doubling/splitting constants.

#33. READ(5,*) IV, NQC(IV,s,ISOT)

If NLDMX(s) > 0 and one has chosen (by setting NDELD ≥ 0) to use the Dunham-type expansions of Eq. (17) or (20) & (22) for the Λ–doubling or $^2\Sigma$ doubling constants, read the orders of the polynomial in $(v + \frac{1}{2})$ used for each rotational order LDMAX(MQO+M,s). If a read-in LDMAX value is < 0, ignore that rotational order.

#34. READ(5,*) (LDMAX(MQO+M,s), M= 1, NLDMX(s))

If the Λ–doubling or $^2\Sigma$ splitting constants are to be represented by Dunham-type expansions and held fixed (IFXLD > 0), loop over the NLDMX(s) rotational orders, and if LDMAX(MQO+M, s) ≥ 0 read the $\{$QLM(L,m,s) $= q_{l,m}^{(1)}\}$ expansion coefficients of Eq. (17) or the $\{\gamma_{l,m}^{(1)}\}$ coefficients of Eq. (20) & (22). If NLDMX(s) or LDMAX(m,s) < 0, ignore the associated READ #35 statement.

$^{\#}$35. `READ(5,*) (QLM(L,MQ0+M,`s`), L=0, LDMAX(MQ0+M,`s`))`

Born-Oppenheimer and JWKB breakdown (BOB) atomic-mass-dependent corrections

If treating data for more than one isotopologue, and one has chosen to allow for BOB breakdown corrections (by setting `BOBORD(`s`)`≥ 0), *and* if one is fitting to determine those parameters for the *first* electronic state considered, must read parameter `BOB00` to specify whether the leading vibrational $\delta_{0,0}^A$ term is to be fitted (`BOB00(`s`)`>0) or omitted (`BOB00(`s`)`≤ 0). The former is usually only appropriate in the rare cases when the data are able to determine the *differences* between the dissociation energies of different isotopologues.

$^{\#}$36. `READ(5,*) BOB00(`s`)`

Next, read the orders `LAMAX(`$atom$`,M,`s`)` of the $(v + \frac{1}{2})$ expansions of Eq. (24) for the first atom, $atom = 1$. Setting a read-in `LAMAX` value <0 causes that order of corrections to be ignored.

$^{\#}$37. `READ(5,*) (LAMAX(`$atom$` = 1,M,`s`), M= 0, BOBORD(`s`))`

If the molecule is heteronuclear, also read the orders `LAMAX(`$atom$` = 2,M,`s`)` of the $(v + \frac{1}{2})$ expansions of Eq. (24) for the second atom, $atom = 2$. For a homonuclear molecule, skip this READ.

$^{\#}$38. `READ(5,*) (LAMAX(`$atom$` = 2,M,`s`), M= 0, BOBORD(`s`))`

If G_v (and hence all BOB correction functions) are held fixed for this state (`IFXGv`>0), loop over the two atoms (for heteronuclear species), and then over rotational order `M=0` to `BOBORD`, reading the expansion coefficients `DELTA(`$atom$`,L,M,`s`)`$= \delta_{l,\mathrm{M}}^{atom}$ of Eq. (24). Note that if one is reading in BOB parameters which are to be held fixed, the minimum power is always $= 0$ in this READ statement, even for the first state considered.

$^{\#}$39. `READ(5,*) (DELTA(`$atom$`,L,M,`s`), L= 0, LAMAX(`$atom$`,M,`s`))`

Generating predictions from a set of fixed known constants

Loop over all bands for which predictions are desired, and for each one read the following. Last band is (assumed to be) end of data file.

$^{\#}$40. `READ(5,*) VP(IBAND),VPP(IBAND),LABLP,LABLP,MN1,MN2,PP,PPP,JMAXX,J2DL,J2DU,J2DD`

> `VP(IBAND)` & `VPP(IBAND)`: are the usual vibrational indices v' and v'', respectively, labeling that band. Set $v' = $`VP(IBAND)`$<0$ to indicate the end of the prediction data set,
>
> `LABLP` & `LABLPP`: are the two-alphanumeric-character names (enclosed in single quotes, as in $'$`X0`$'$) identifying the upper and lower electronic state for which the predicted band is to be generated. Set `LABLP`$=$`LABLPP` to generate IR or MW transitions for that state.
>
> `MN1` & `MN2`: are the integer mass numbers identifying the isotopologue for which the predictions are to be generated.
>
> `PP` & `PPP`: are integers with values $+1$, 0 or -1 to indicate the e/f parity of the upper ($p' = $`PP`) and lower ($p'' = $`PPP`) levels in the band.
>
> `JMAXX, J2DL, J2DU` & `J2DD`: generate predicted transition energies for $J'' = 0$ to `JMAXX` subject to the selection rule that $\Delta J = J' - J''$ runs from `J2DL` to `J2DU` in steps of `J2DD`.

D. Illustrative Cases and Their Input Data Files

This program has been successfully applied to a wide range of cases.[5,17,23,52–54,57,60,62–67] The following subsections briefly describe a selection of those cases, present the associated channel–5 instruction data files, and indicate the associated CPU time requirements.

1.   Dunham and BOB-Correction Combined-Isotopologue Fit to MW & IR Data for HF & DF

The first illustrative case considered here is the relatively straightforward combined-isotopologue analysis of pure rotational microwave transitions and vibration-rotation infrared transitions for the ground electronic state of HF and DF, as reported in Ref. 5. In order to have the output (see Appendix B) illustrate the nature of the output associated with the sequential rounding procedure, print-control parameter LPRINT was set at a moderately high level of 3. This non-linear least-squares fit of 36 parameters to 722 data required 0.56 sec of CPU time on an SGI Origin-200.

```
1 9  0  2  1                  %  AN(1) AN(2) CHARGE NISTP NSTATES
 'HFDF.4'                     %  DATAFILE
10.d0  1  0  3  0             %  UCUTOFF IROUND ROBUST LPRINT PRINP
1  19                         %  MN(1,ISOT=1) MN(2,ISOT=1)
2  19                         %  MN(1,ISOT=2) MN(2,ISOT=2)
'X0' 0  200  0  0 5           % SLABL IOMEG JTRUNC EFSEL VMIN VMAX
5  0 0 0  0 0 0    4          % NCDC NDEGv NDEBv NDECDC IFXGv IFXBv IFXCDC BOBORD
 5                            %  LMAX(0) ... G(v) Dunham expansion powers
 5                            %  LMAX(1) ... Bv Dunham expansion powers
 4  3  2  1  0                %  LMAX(2) LMAX(3) LMAX(4) LMAX(5) LMAX(6)
 0                            %  BOB00
 3  2  1  1 -1                %  LAMAX(1,0) LMAXA(1,1) ... BOB corrn powers for H
-1 -1 -1 -1 -1                %  LAMAX(2,0) LMAXA(2,1) ... BOB corrn powers for F
```

2.   NDE Fit to PFOODR Data for the $1\,^3\Sigma_g^-$ State of Na_2

The second case considered here is the channel–5 input data file for the analysis of the $1\,^3\Sigma_g^-$ state of Na_2 reported in Ref. 23. The double-resonance PFOODR experimental data for this case were treated as if they involved transitions into a $^1\Sigma_g^-$ state (i.e., the unresolved spin splitting was ignored). The data were also expressed as transitions from the ground state $v = -1/2$ level, so while formally a 2-state analysis (NSTATES = 2), the vibration-rotation energies of the ground state were generated from the molecular constants: $\omega_e \equiv Y_{1,0} = 0.0 = B_e \equiv Y_{0,1}$, which were held fixed: IFXGv(1) = IFXBv = IFXCDC(1) = 1 .

The term values for the upper (state $s=2$) electronic state were represented by NDE functions for G_v and B_v, and those NDE functions were optimized by the fit. At the same time, the CDCs were held fixed at numerically calculated read-in band-constant values, so this data file had to include a full listing of those CDCs. These CDCs were generated separately (using program LEVEL [35]) from an RKR potential calculated [32] from the pure NDE G_v and B_v expressions yielded by the iterative self-consistent procedure described in Section II.C.2. This final fit was performed with $v_{\mathfrak{D}}$ fixed at the rounded-off value yielded by a previous fit in which $v_{\mathfrak{D}}$ was allowed to vary. This non-linear least-squares fit of 12 parameters to 515 data required 0.14 sec of CPU time on an SGI Origin-200.

```
11 11  0  1 2                 %  AN(1) AN(2) CHARGE NISTP NSTATES
'Na2.4'                       %  DATAFILE
90.d0  1  0  -1  0            %  UCUTOFF IROUND ROBUST LPRINT PRINP
23  23                        %  MN(1,ISOT=1)  MN(2,ISOT=1)
'X0' 0  200  0  0 0           %(1) SLABL IOMEG JTRUNC EFSEL VMIN VMAX
0  0 0 0  1 1 1   -1          %(1) NCDC NDEGv NDEBv NDECDC IFXGv IFXBv IFXCDC BOBORD
 1                            %(1) LMAX(1): order of Gv expansion
0.d0                          %(1) T0
0.d0                          %(1) we = Y_{1,0}
 0                            %(1) LMAX(2): order Bv expansion
0.d0                          %(1) Be = Y_{0,1}
'3S' 0  200  0  0 57          %(2) SLABL IOMEG JTRUNC EFSEL VMIN VMAX
4  1 1 -1  0 0 1   -1         %(2) NCDC NDEGv NDEBv NDECDC IFXGv IFXBv IFXCDC BOBORD
6 39951.591d0  61.41d0   2.05774d7  5     %(2) NLR DLIMIT vD Cn NSIG
1  3  2  1  1                 %(2) ITYPE NP0 NQ0 IP0 IQ0
4.49455D-01 -3.65200D-03 1.60000D-05      %(2) PM0's
4.97000D-02 1.40000D-02      %(2) QM0's
 1   1                        %(2) IFXD  IFXvD
 3  7  0  1  1                %(2) ITYPB NP1 NQ1 IP1 IQ1
1.334D-01 -1.6653D-02 9.0D-04 -2.722D-05
```

```
      4.72400D-07 -4.39436D-09 1.70000D-11       %(2) PM1's
      0  -7.41928D-07  1.20818D-12  2.55149D-17  4.36463D-21 -8.70940D-26 -3.16153D-30
      1  -7.21605D-07  3.70130D-12 -6.90471D-17  2.06409D-21 -3.79350D-27  1.46903D-31
      2  -7.13958D-07  5.31008D-12 -1.13974D-16  5.05754D-22  5.87043D-26 -6.43137D-31
      3  -7.13809D-07  6.20389D-12 -1.22458D-16 -8.74113D-22  1.01772D-25 -1.37230D-30
      ...... omit 50 similar lines listing CDC constants for v(A3)= 4 to 53 ..........
     54  -2.69835D-06 -2.21373D-10 -4.34372D-14 -1.19404D-17 -3.84374D-21 -1.24311D-24
     55  -3.08187D-06 -3.25742D-10 -8.52296D-14 -3.12703D-17 -1.33759D-20 -6.05374D-24
     56  -3.58165D-06 -5.16224D-10 -1.86723D-13 -9.08733D-17 -5.24538D-20 -3.65265D-23
     57  -4.23459D-06 -8.97096D-10 -5.61412D-13 -5.34870D-16 -5.42782D-19 -5.11158D-22
```

3. Dunham & Band Constant Fit to Chemiluminescence (and Other Data) for 3 Isotopologues of BaO

The final illustrative case considered here is a fit to MW, IR, electronic fluorescence and chemiluminescence data for the four isotopologues ^{138}Ba^{16}O, ^{137}Ba^{16}O, ^{136}Ba^{16}O and ^{135}Ba^{16}O (see Ref. 52). A fragment of the input experimental data file for this case was presented at the end of Section IV.A. For this case, the most abundant isotopologue ^{138}Ba^{16}O was chosen as the reference species ($\alpha = 1$),[52] so its mass numbers are read first. For the ground $X^1\Sigma^+$ electronic state ('X0') the term values were represented by Dunham expansions for all of G_v & B_v and the CDCs. Unperturbed levels associated with $v' = 0$ in the excited $A^1\Sigma^+$ state ('A0') were represented by band constants, with three rotational constants (NRC = 3) being used for each of the first two isotopologues (^{138}BaO and ^{137}BaO), for which relatively more data are available, and two for the others. The more highly perturbed $v' \geq 1$ levels of the $A^1\Sigma^+$ state were then represented by individual term values $\{T^{(\alpha)}(v', J', p')\}$.

In the original work,[52] the term-value representation for $v' \geq 1$ levels of the $A^1\Sigma^+$ was accomplished by rearranging the data involving those levels as fluorescence series. However, DParFit now allows one to input such data in normal electronic vibrational band format, as long as those data are given a distinct electronic-state label and the associated input parameter NDEGv is assigned the value -2. For the case of BaO, the "regular" data involving $A^1\Sigma^+$-state level $v' = 0$ which are to be represented by band constants are identified as belonging to electronic state A0, for which input parameters NDEGv, NDEBv and NDECDC all have the values -1. Data involving the the more heavily perturbed $v' \geq 1$ levels which are to be represented by individual term values are then identified as belonging to a different electronic state labelled as Ap, for which state one reads in NDEGv $= -2$. In other words, although only two electronic states are directly involved in the chemiluminescence spectrum, we read in NSTATES $= 3$, and treat bands involving A-state levels $v' \geq 1$ as if they actually belonged to a different electronic state.

The resulting fit of 13,683 data to determine 1,400 sequentially-rounded parameters (12 X–state Dunham constants, 14 A–state band constants and 1,372 term values and 2 fluorescence series origins) using the conventional band-format representation of the perturbed $v(A)' \geq 1$ data, yields exactly the same results reported in Ref. 52. This fit required 209 min of CPU time on an SGI Origin-200. This relatively large amount of CPU time is due to the large number (1,400!) of parameters being fitted and sequentially rounded, and not to the large number of data. In contrast, the 12–parameter fit to 5,227 data for 5 isotopologues of GeO described in Ref. 64 required only 0.85 sec of CPU time. The CPU time required for this BaO fit is reduced to 37.5 min if no parameter rounding is done; this CPU time reduction is relatively modest because the program rounds all individual term values and fluorescence series in one step, so the repetitious sequential rounding is only done for the 26 Dunham-type and band-constant parameters. A compressed version of the main channel–6 output for this case is presented in Appendix B.

```
 56 8  0  4  3           %  AN(1) AN(2) CHARGE NISTP NSTATES
  'BaOband.4'            %  FILENAME
  9.d0  -1  0 -1  0      %  UCUTOFF IROUND ROBUST LPRINT PRINP
 138  16                 %  MN(1,ISOT=1) MN(2,ISOT=1)
 137  16                 %  MN(1,ISOT=2) MN(2,ISOT=2)
 136  16                 %  MN(1,ISOT=3) MN(2,ISOT=3)
 135  16                 %  MN(1,ISOT=4) MN(2,ISOT=4)
 'X0'  0  200  0  0 35   %(1) SLABL IOMEG JTRUNC EFSEL VMIN VMAX
 6  0 0 0  0 0 0  -1     %(1) NCDC NDEGv NDEBv NDECDC IFXGv IFXBv IFXCDC BOBORD
```

```
 5                      %(1) LMAX(0) 5th order of Gv
 3                      %(1) LMAX(1) 3th order of Bv
 2  -1  -1 -1 -1 -1     %(1) LMAX(2) 2nd of Dv, LMAX(3), ...
 'A0' 0  200  0  0 0    %(2) SLABL IOMEG JTRUNC EFSEL VMIN VMAX
 6 -1 -1 -1  0 0 0  -1  %(2) NCDC NDEGv NDEBv NDECDC IFXGv IFXBv IFXCDC BOBORD
 0 1 3 0                %(2) v FITGV NRC NQC for v'=0  ISOT=1
 0 1 3 0                %(2) v FITGV NRC NQC for v'=0  ISOT=2
 0 1 2 0                %(2) v FITGV NRC NQC for v'=0  ISOT=3
 0 1 2 0                %(2) v FITGV NRC NQC for v'=0  ISOT=4
 'Ap' 0  200  0  0 99   %(3) SLABL IOMEG JTRUNC EFSEL VMIN VMAX
 6 -2 -2 -2  0 0 0  -1  %(3) NCDC NDEGv NDEBv NDECDC IFXGv IFXBv IFXCDC BOBORD
```

Acknowledgements

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[2] This program name differs slightly from that associated with early versions of this code[3] ("DSParFit") because the present version is no longer restricted to the treatment of data for *Singlet* states.

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[56] Note that the expression for $Y_{0,0}$ on p. 109 of Ref. 4 should read: $Y_{0,0} = (Y_{0,1} + Y_{2,0})/4 - [(Y_{1,1} Y_{1,0})/(12 Y_{0,1})] + [(Y_{1,1} Y_{1,0})/(12 Y_{0,1})]^2 / Y_{0,1}$, and that the relation $Y_{l,m} \equiv \frac{\partial^l}{\partial v^l} \frac{\partial^m E(v,J)}{\partial[J(J+1)]^m}\Big|_{J=0,v=-1/2}$ 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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Appendix A. Program Structure

The present section lists the names and outlines the functions of the various subroutines used by DParFit, and indicates their hierarchy. In particular, the level of indentation in this list indicates which subroutines call which others.

DPARFIT: The main program which reads the input data characterizing the molecular system and the type of fit to be performed, calls the actual fitting routines, and prints descriptions of the system and the results.

> **MASSES:** A data subroutine containing accurate atomic masses (and other properties) of all stable atomic isotopes. Its presence obviates the need for a user to look up and type precise particle masses into the input data file.

> **READATA:** The data input subroutine for reading in (on channel–4) and arranging and characterizing the experimental data to be used in the fit.

> **NDEXM:** For a molecular state whose vibration-rotation energies are to be represented by NDE functions, calculates the theoretical limiting behaviour coefficients $X_m(n, C_n)$ of Eq. (9).

> **NDEDGB:** For a molecular state represented by NDE functions, calculates G_v and B_v and (components of) their partial derivatives w.r.t. various expansion parameters.

> **TVSORT:** If fitting to individual term values for a given electronic state, sorts through the global data file and identifies the particular term value(s) associated with each transition involving level(s) of this state.

> **NLLSSRR:** A general linear or non-linear least-squares fitting subroutine package which can also implement (when input parameter $\texttt{IROUND} \neq 0$) the "sequential rounding and refitting" procedure of Ref. 60).

>> **DYIDPJ:** The key user-supplied subroutine required by **NLLSSRR**, which for each datum returns the calculated value and partial derivatives with respect to all parameters of the model for the current set of trial parameters.

>>> **MAPPAR:** A subroutine called by **DYIDPJ** at the beginning of each fitting cycle to map the generic parameters used internally by **NLLSSRR** onto the actual physical parameters of the model used in the fit.

>>> **PREDICT:** A subroutine using the current band constants and vibrational level Λ-doubling constants to calculate the value of each datum.

>>> **NDEDGB:** For NDE representations of G_v and B_v, calculates their values and their partial derivatives w.r.t. various parameters required by the general partial derivative subroutine **DYIDPJ**.

> **PPISOT:** For Dunham expansion representations, generates $\{Y_{l,m}^{(\alpha)}\}$ parameters for the minority isotopologues, each rounded at the first significant digit of the parameter sensitivity.[60]

> **NDEDUN:** For NDE representations of G_v and B_v, generates the conventional Dunham expansion parameters $\{\omega_e, \omega_e x_e, B_e$ & $\alpha_e\}$ and their derivatives w.r.t. the NDE expansion parameters, from the G_v and B_v NDE functions and their derivatives.

> **DIFFSTATS:** On completion of a fit, summarizes dimensionless RMS deviations for the entire data set on a band-by-band basis.

> **MKPREDICT:** If the input parameter (see READ $^\#2$) **DATAFILE** is equal to $'$MAKEPRED$'$, reads input to cause the program to prediction transitions for specified bands which are generated from by a complete fixed set of molecular-state parameters.

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1. Output for a Combined-Isotopologue Dunham and BOB-Correction Analysis of MW and IR Data for HF

A somewhat truncated version of the channel–6 output file for the combined-isotopologue fit to MW and IR data for HF and DF, as reported in Ref. 5.

```
Input data for  2  isotopomer(s)
*******************************
    Isotopomer       Mass of atom-1    Mass of atom-2      Reduced mass
  --------------     --------------    --------------     --------------
  H(  1)- F( 19)      1.0078250319      18.9984032000      0.9570552774
  H(  2)- F( 19)      2.0141017779      18.9984032000      1.8210450255

Use experimental data input file:  HFDF.4

Apply "Sequential Rounding & Refitting" at digit-1 of the (local) parameter
    uncertainty, selecting remaining parameter with largest relative uncertainty

Fit uses standard  1/[uncertainty(i)]**2  data weighting

State X0 is a Singlet with  Omega= 0
********************  so rotational energies depend on powers of  [J(J+1)- 0]

Neglect data with: Uncertainties > UCUTOFF=    10.0     (cm-1)
      and State X0 data with  J > JTRUNC= 200  or  v  outside range  0  to   5

Absolute zero of energy is fixed at  G(v"=-1/2)  of  State X0
***********************

Fit for State X0  Gv's  uses Dunham expansion of order  5
*********************

Fit for State X0  Bv's  uses Dunham expansion of order  5
*********************

Dunham Fit for State X0  uses  CDC(1)=-Dv  expansion of order  4
=======================        CDC(2)= Hv  expansion of order  3
                               CDC(3)= Lv  expansion of order  2
                               CDC(4)= Mv  expansion of order  1
                               CDC(5)= Nv  expansion of order  0
Fit State X0  " Gv" BOB corrections for  H  to Dunham expansion of order:  3
                  while IGNORING the constant  delta(0,0)  term
Fit State X0  " Bv" BOB corrections for  H  to Dunham expansion of order:  2
Fit State X0  "-Dv" BOB corrections for  H  to Dunham expansion of order:  1
Fit State X0  " Hv" BOB corrections for  H  to Dunham expansion of order:  1
Full  2-cycle convergence:  Max{|change/sens.|}= 9.8D-05 < 1    DRMSD=  8.53D-01

   722 data fit to    36 param. yields    DRMS(devn)= 0.8533       tst(PS)= 9.8D-05
    PV(    1) =  4.13838509021990D+03 (+/- 1.3D-03)     PS= 6.0D-07    PC=-7.3D-12
    PV(    2) = -8.99432415810432D+01 (+/- 1.4D-03)     PS= 2.5D-07    PC= 1.1D-11
    PV(    3) =  9.24504125752426D-01 (+/- 6.1D-04)     PS= 6.3D-08    PC=-4.2D-12
..... omit printout for the next 30 parameters ............................
    PV(   34) = -1.25224979707589D-07 (+/- 1.9D-08)     PS= 1.0D-10    PC=-7.2D-18
    PV(   35) = -1.91781830756539D-10 (+/- 1.7D-11)     PS= 1.3D-13    PC= 7.4D-20
    PV(   36) =  5.98435768820212D-11 (+/- 2.0D-11)     PS= 1.4D-13    PC= 4.3D-21
================================================================================
Round Off  PV(  26)= -6.95067694938811D-20 (+/- 3.84D-20)     PS= 1.06D-23
        fix it as  -7.0000000000000D-20  & refit:  DRMS(deviations)= 8.533D-01
Full  1-cycle convergence:  Max{|change/sens.|}= 1.6D-04 < 1    DRMSD=  8.53D-01
================================================================================
Round Off  PV(  19)= -5.3915557064136D-11 (+/- 2.09D-11)     PS= 6.25D-15
        fix it as  -5.0000000000000D-11  & refit:  DRMS(deviations)= 8.533D-01
Full  1-cycle convergence:  Max{|change/sens.|}= 1.6D-04 < 1    DRMSD=  8.53D-01
================================================================================
Round Off  PV(  36)=  6.1128687470853D-11 (+/- 1.86D-11)     PS= 1.53D-13
        fix it as   6.0000000000000D-11  & refit:  DRMS(deviations)= 8.534D-01
Full  1-cycle convergence:  Max{|change/sens.|}= 6.2D-05 < 1    DRMSD=  8.53D-01
================================================================================
..... omit printout of stepwise rounding results for the next 30 parameters ...
================================================================================
Round Off  PV(   2)= -8.9943188833036D+01 (+/- 1.26D-05)     PS= 2.92D-06
        fix it as  -8.9943190000000D+01  & refit:  DRMS(deviations)= 8.546D-01
Full  1-cycle convergence:  Max{|change/sens.|}= 3.8D-08 < 1    DRMSD=  8.55D-01
================================================================================
Round Off  PV(   6)=  2.0953712032552D+01 (+/- 4.72D-07)     PS= 3.22D-07
        fix it as   2.0953712000000D+01  & refit:  DRMS(deviations)= 8.546D-01
Full  1-cycle convergence:  Max{|change/sens.|}= 4.3D-08 < 1    DRMSD=  8.55D-01
================================================================================
Round Off  PV(   1)=  4.1383850255438D+03 (+/- 1.54D-05)     PS= 2.10D-05
        fix it as   4.1383850300000D+03  & refit:  DRMS(deviations)= 8.546D-01

   722 data fit to    36 param. yields    DRMS(devn)= 0.8548
    PV(    1) =  4.13838503000000D+03 (+/- 1.4D-03)     PS= 6.0D-07    PC= 6.0D-05
    PV(    2) = -8.99431900000001D+01 (+/- 1.4D-03)     PS= 2.5D-07    PC=-5.2D-05
    PV(    3) =  9.24488000000001D-01 (+/- 6.1D-04)     PS= 6.3D-08    PC= 1.6D-05
..... omit printout for the next 30 parameters ............................
    PV(   34) = -1.26000000000000D-07 (+/- 1.9D-08)     PS= 1.0D-10    PC= 7.8D-10
    PV(   35) = -1.90000000000000D-10 (+/- 1.7D-11)     PS= 1.3D-13    PC=-1.8D-12
    PV(   36) =  6.00000000000001D-11 (+/- 2.0D-11)     PS= 1.4D-13    PC=-1.6D-13

After Sequential Rounding & Refitting,  fit of    36 parameters to   722 data
******************************************  yields    DSE= 0.8769

State X0  Dunham expansion Gv parameters:
        YLM( 1,0)=  4.138385030000D+03 (+/- 1.4D-03)     Sensitivity= 6.0D-07
        YLM( 2,0)= -8.994319000000D+01 (+/- 1.4D-03)     Sensitivity= 2.5D-07
        YLM( 3,0)=  9.244880000000D-01 (+/- 6.1D-04)     Sensitivity= 6.3D-08
```

```
                YLM( 4,0)= -1.549500000000D-02 (+/- 1.2D-04)     Sensitivity= 1.2D-08
                YLM( 5,0)= -4.390000000000D-04 (+/- 8.1D-06)     Sensitivity= 2.1D-09
State X0   Dunham expansion Bv parameters:
                YLM( 0,1)=  2.095371200000D+01 (+/- 4.1D-06)     Sensitivity= 1.8D-08
                YLM( 1,1)= -7.933704000000D-01 (+/- 1.3D-05)     Sensitivity= 7.1D-09
                YLM( 2,1)=  1.092440000000D-02 (+/- 1.2D-05)     Sensitivity= 1.9D-09
                YLM( 3,1)= -2.192900000000D-04 (+/- 4.8D-06)     Sensitivity= 4.1D-10
                YLM( 4,1)= -3.200000000000D-06 (+/- 8.4D-07)     Sensitivity= 7.9D-11
                YLM( 5,1)= -4.880000000000D-07 (+/- 5.4D-08)     Sensitivity= 1.5D-11
State X0   Dunham expansion CDC(1) parameters:
                YLM( 0,2)= -2.148911800000D-03 (+/- 2.7D-08)     Sensitivity= 3.3D-11
                YLM( 1,2)=  5.851740000000D-05 (+/- 3.7D-08)     Sensitivity= 1.4D-11
                YLM( 2,2)= -1.107100000000D-06 (+/- 2.4D-08)     Sensitivity= 4.5D-12
                YLM( 3,2)= -2.800000000000D-08 (+/- 6.2D-09)     Sensitivity= 1.1D-12
                YLM( 4,2)= -4.340000000000D-09 (+/- 5.4D-10)     Sensitivity= 2.5D-13
State X0   Dunham expansion CDC(2) parameters:
                YLM( 0,3)=  1.659810000000D-07 (+/- 1.0D-10)     Sensitivity= 2.5D-14
                YLM( 1,3)= -4.606000000000D-09 (+/- 6.2D-11)     Sensitivity= 1.6D-14
                YLM( 2,3)= -5.000000000000D-11 (+/- 2.1D-11)     Sensitivity= 6.1D-15
                YLM( 3,3)= -2.340000000000D-11 (+/- 2.6D-12)     Sensitivity= 1.9D-15
State X0   Dunham expansion CDC(3) parameters:
                YLM( 0,4)= -1.540200000000D-11 (+/- 1.8D-13)     Sensitivity= 1.9D-17
                YLM( 1,4)=  2.600000000000D-13 (+/- 5.5D-14)     Sensitivity= 1.4D-17
                YLM( 2,4)= -5.900000000000D-14 (+/- 6.4D-15)     Sensitivity= 6.0D-18
State X0   Dunham expansion CDC(4) parameters:
                YLM( 0,5)=  1.340000000000D-15 (+/- 1.4D-16)     Sensitivity= 1.4D-20
                YLM( 1,5)= -9.800000000000D-17 (+/- 1.8D-17)     Sensitivity= 1.1D-20
State X0   Dunham expansion CDC(5) parameters:
                YLM( 0,6)= -7.000000000000D-20 (+/- 3.8D-20)     Sensitivity= 1.1D-23
State X0   Born-Oppenheimer breakdown parameters:
              delta( H; 1,0)= -1.139000000000D-01 (+/- 8.4D-04)     Sensitivity= 1.7D-06
              delta( H; 2,0)= -4.800000000000D-03 (+/- 5.0D-04)     Sensitivity= 9.6D-07
              delta( H; 3,0)= -9.400000000000D-04 (+/- 8.4D-05)     Sensitivity= 3.5D-07
              delta( H; 0,1)= -6.035000000000D-03 (+/- 4.0D-06)     Sensitivity= 5.5D-08
              delta( H; 1,1)=  3.730000000000D-04 (+/- 5.7D-06)     Sensitivity= 2.8D-08
              delta( H; 2,1)= -1.200000000000D-05 (+/- 1.2D-06)     Sensitivity= 1.1D-08
              delta( H; 0,2)=  1.910000000000D-06 (+/- 1.9D-08)     Sensitivity= 1.6D-10
              delta( H; 1,2)= -1.260000000000D-07 (+/- 1.9D-08)     Sensitivity= 1.0D-10
              delta( H; 0,3)= -1.900000000000D-10 (+/- 1.7D-11)     Sensitivity= 1.3D-13
              delta( H; 1,3)=  6.000000000000D-11 (+/- 2.0D-11)     Sensitivity= 1.4D-13


State-X0 Sensitivity-Rounded YLM's for Minority Isotopomers:
     ============================================================
       H(  2)- F( 19)

Zero point level T(v=0) relative to v= -1/2 of the first state considered (X0)
    for the reference isotopomer is:    2046.821296
    and for the others:    1488.266832

Semiclassica  Y00  of the reference isotopomer is:  3.947346( 0.000393)
    & of others:  2.072828( 0.000083)

            YLM( 1,0)  3.00008176820D+03 (9.0D-04)
            YLM( 2,0) -4.72711540000D+01 (7.1D-04)
            YLM( 3,0)  3.52050620000D-01 (2.3D-04)
            YLM( 4,0) -4.27980800000D-03 (3.2D-05)
            YLM( 5,0) -8.79033000000D-05 (1.6D-06)

            YLM( 0,1)  1.10106969800D+01 (2.0D-06)
            YLM( 1,1) -3.02202795000D-01 (4.5D-06)
            YLM( 2,1)  3.01572600000D-03 (3.3D-06)
            YLM( 3,1) -4.39096200000D-05 (9.5D-07)
            YLM( 4,1) -4.64510000000D-07 (1.2D-07)
            YLM( 5,1) -5.13540000000D-08 (5.7D-09)

            YLM( 0,2) -5.93278170000D-04 (7.4D-09)
            YLM( 1,2)  1.17046500000D-05 (7.0D-09)
            YLM( 2,2) -1.60707400000D-07 (3.5D-09)
            YLM( 3,2) -2.94660000000D-09 (6.6D-10)
            YLM( 4,2) -3.31100000000D-10 (4.1D-11)

            YLM( 0,3)  2.40801400000D-08 (1.5D-11)
            YLM( 1,3) -4.81554000000D-10 (6.4D-12)
            YLM( 2,3) -3.81450000000D-12 (1.6D-12)
            YLM( 3,3) -1.29420000000D-12 (1.4D-13)

            YLM( 0,4) -1.17501200000D-12 (1.4D-14)
            YLM( 1,4)  1.43796000000D-14 (3.0D-15)
            YLM( 2,4) -2.36560000000D-15 (2.6D-16)

            YLM( 0,5)  5.37262000000D-17 (5.4D-18)
            YLM( 1,5) -2.84850000000D-18 (5.4D-19)

            YLM( 0,6) -1.47500000000D-21 (8.1D-22)


     ==================================================================
     *** Discrepancies for   11 bands/series of  H(  1)- F( 19) ***
     ==================================================================


     ==================================================================
      112 State X0  H(  1)- F( 19) MW transitions in   5 vib. levels
     ================================================= Avge. ========
```

```
      v'  v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
     -------------------------------------------------------------------
      0   0    34      0     35    4.0D-04   2.0D-03    0.23031   0.845
      1   1    25     12     35    4.9D-04   1.5D-03    0.03644   0.852
      2   2    29     13     33    8.3D-04   3.0D-03   -0.27997   0.801
      3   3    17     13     30    5.9D-04   2.0D-03   -0.23610   0.721
      4   4     7     15     22    7.1D-04   1.0D-03   -0.40570   1.209
     -------------- For these   112 lines, overall:   -0.05564   0.846

     ================================================================
     214 State X0  H(  1)- F( 19) InfraRed transitions in    6 bands
     ================================================================
                                                 ===== Avge. ========
      v'  v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
     -------------------------------------------------------------------
      1   0    56      0     28    3.7D-04   2.0D-03   -0.01667   0.745
      2   1    46      0     26    5.7D-04   2.0D-03   -0.19937   0.880
      3   2    40      0     24    5.8D-04   2.0D-03   -0.02713   0.969
      4   3    35      0     22    6.1D-04   2.0D-03   -0.10491   0.714
      5   4    20      1     17    6.5D-04   2.0D-03    0.11635   1.120
      3   0    17      0     10    2.0D-03   2.0D-03    1.63158   1.745
     -------------- For these   214 lines, overall:    0.07104   0.964

     ================================================================
     *** Discrepancies for    9 bands/series of  H(  2)- F( 19) ***
     ================================================================

     ================================================================
     115 State X0  H(  2)- F( 19) MW transitions in    4 vib. levels
     ================================================================
                                                 ===== Avge. ========
      v'  v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
     -------------------------------------------------------------------
      0   0    50      0     48    5.3D-04   1.0D-03   -0.04780   0.780
      1   1    38     10     44    5.4D-04   1.0D-03   -0.22605   0.944
      2   2    21     11     39    7.0D-04   1.0D-03   -0.26470   0.878
      3   3     6     27     33    1.0D-03   1.0D-03   -0.54287   0.924
     -------------- For these   115 lines, overall:   -0.17214   0.863

     ================================================================
     281 State X0  H(  2)- F( 19) InfraRed transitions in    5 bands
     ================================================================
                                                 ===== Avge. ========
      v'  v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
     -------------------------------------------------------------------
      1   0    89      0     32    5.9D-04   5.0D-03   -0.02298   0.629
      2   1    85      0     30    6.7D-04   2.0D-03    0.08949   0.830
      3   2    59      0     24    6.4D-04   2.0D-03   -0.05315   0.795
      4   3    32      0     22    5.9D-04   2.0D-03   -0.03217   0.680
      5   4    16      2     18    5.0D-04   5.0D-04    0.14896   1.033
     -------------- For these   281 lines, overall:    0.01345   0.761

     ======================================================
     For overall fit to   722 data,  DRMS(deviations)= 0.8548
     ======================================================
```

2.   Output for an NDE Analysis of PFOODR Data for the $1\,^3\Sigma_g^+$ State of Na$_2$

A truncated copy of the channel-6 output file for the fit to PFOODR data for the $1\,^3\Sigma_g^+$ State of Na$_2$ using NDE functions for G_v and B_v and fixed, numerically-calculated CDCs, as reported in Ref. 23.

```
     Input data for  1  isotopomer(s)
     ********************************
        Isotopomer      Mass of atom-1   Mass of atom-2    Reduced mass
     ---------------    --------------   --------------   --------------
     Na( 23)-Na( 23)     22.9897696600    22.9897696600    11.4948848300

     Use experimental data input file: Na2.4

     Apply "Sequential Rounding & Refitting" at digit-1 of the (local) parameter
        uncertainty, selecting remaining parameter with largest relative uncertainty

     Fit uses standard  1/[uncertainty(i)]**2  data weighting

     State X0 is a Singlet with  Omega= 0
     ********************* so rotational energies depend on powers of  [J(J+1)- 0]

     Fixed State X0  Gv for Isot.-1 defined relative to  T(v=-1/2)=     0.00000 cm-1
     Fixed State X0  Gv  values defined by isotopomer-1 Dunham coefficients:
      0.000000000000D+00
     Fixed State X0  Bv  values defined by isotopomer-1 Dunham coefficients:
      0.000000000000D+00

     State X0  Constants for  Na( 23)-Na( 23)  held fixed at values:
        v      Gv         Bv
     -------------------------
        0     0.00000  0.00000000

     State 3S is a Singlet with  Omega= 0
     ********************* so rotational energies depend on powers of  [J(J+1)- 0]

     NDE function(s) for State 3S which has potential tail:  D - 2.057740D+07/R**6
        & initial parameters:   D(limit) = 39951.5910    and
       vD(ISOT=1)= 61.41000000     based on factors  XM(m,ISOT):
           XM(0,1)=  4.486700D-02
           XM(1,1)=  3.092100D-03

     State 3S NDE for Gv represented by  (NP= 3/NQ= 2)  Outer Pade NDE  in  (vD-v)
     ------------------ with leading numerator and denominator powers  1 & 1
           where for Isotopomer-1  vD= 61.41000   and   DLIMIT= 39951.5910
        Input numerator coefficients:   4.4945500000000D-01 -3.6520000000000D-03
```

37

```
                   1.6000000000000D-05
        Input denominator coefficients:  4.9700000000000D-02  1.4000000000000D-02

State 3S NDE for Bv represented by  (NP= 7/NQ= 0) Exponential NDE  in  (vD-v)
------------------  with leading numerator and denominator powers  1 &  1
     Input numerator coefficients:    1.3340000000000D-01 -1.6653000000000D-02
                 9.0000000000000D-04 -2.7220000000000D-05  4.7240000000000D-07
                -4.3943600000000D-09  1.7000000000000D-11

Fix State 3S  CDC's  at read-in values

State 3S  Constants for  Na( 23)-Na( 23)  held fixed at values:
  v   CDC(1)=-Dv   CDC(2)= Hv   CDC(3)= Lv   CDC(4)= Mv  CDC(
 ----------------------------------------------------
  0 -7.41928D-07  1.20818D-12  2.55149D-17  4.36463D-21
  1 -7.21605D-07  3.70130D-12 -6.90471D-17  2.06409D-21
  2 -7.13958D-07  5.31008D-12 -1.13974D-16  5.05754D-22
.....  Omit input CDC's for the next 53 levels ..........
 56 -3.58165D-06 -5.16224D-10 -1.86723D-13 -9.08733D-17
 57 -4.23459D-06 -8.97096D-10 -5.61412D-13 -5.34870D-16

Neglect data with: Uncertainties > UCUTOFF=    90.0     (cm-1)
      and State X0 data with  J > JTRUNC= 200  or  v  outside range  0  to   0
      and State 3S data with  J > JTRUNC= 200  or  v  outside range  0  to  57

Fit State 3S  Gv's to NDE or MXS function while fixing   DLIMIT= 39951.59100
**************************************
State 3S  Gv's  initially defined by  (NP= 3/NQ= 2)  Outer Pade NDE  in  (vD-v)
------------  with leading numerator and denominator powers  1 &  1
              where for Isotopomer-1   vD=  61.41000000
     Input numerator coefficients:    4.4945500000000D-01 -3.6520000000000D-03
                 1.6000000000000D-05
     Input denominator coefficients:  4.9700000000000D-02  1.4000000000000D-02
State 3S  Bv's  initially defined by  (NP= 7/NQ= 0) Exponential NDE  in  (vD-v)
------------  with leading numerator and denominator powers  1 &  1
     Input numerator coefficients:    1.3340000000000D-01 -1.6653000000000D-02
                 9.0000000000000D-04 -2.7220000000000D-05  4.7240000000000D-07
                -4.3943600000000D-09  1.7000000000000D-11

   515 data fit to   12 param. yields   DRMS(devn)= 1.029      tst(PS)= 2.1D-01
   PV(   1) =  4.38613433877767D-01 (+/- 1.1D-02)   PS= 3.0D-07   PC=-1.1D-08
   PV(   2) = -3.55168069234957D-03 (+/- 1.3D-04)   PS= 5.6D-09   PC= 1.1D-10
   PV(   3) =  1.55234937541121D-05 (+/- 7.0D-07)   PS= 1.0D-10   PC=-5.7D-13
   PV(   4) =  4.85049338684768D-02 (+/- 2.8D-03)   PS= 7.2D-07   PC=-2.4D-09
   PV(   5) =  1.37042062768483D-02 (+/- 2.6D-04)   PS= 1.4D-08   PC=-2.8D-10
   PV(   6) =  1.34927181950256D-01 (+/- 5.8D-03)   PS= 5.5D-07   PC=-1.3D-09
   PV(   7) = -1.70156484795586D-02 (+/- 1.1D-03)   PS= 1.1D-08   PC=-4.7D-11
   PV(   8) =  9.31322135935990D-04 (+/- 8.5D-05)   PS= 2.2D-10   PC= 1.4D-11
   PV(   9) = -2.85420664703166D-05 (+/- 3.3D-06)   PS= 4.3D-12   PC=-7.4D-13
   PV(  10) =  5.01480767746927D-07 (+/- 6.9D-08)   PS= 8.0D-14   PC= 1.7D-14
   PV(  11) = -4.71831215944650D-09 (+/- 7.5D-10)   PS= 1.5D-15   PC=-1.7D-16
   PV(  12) =  1.84371050129198D-11 (+/- 3.3D-12)   PS= 2.7D-17   PC= 7.0D-19

After Sequential Rounding & Refitting,  fit of   12 parameters to  515 data
************************************   yields    DSE= 1.041

State 3S  NDE  Gv  function is a  (NP= 3/NQ= 2)  Outer Pade NDE  in  (vD-v)
              with leading numerator and denominator powers  1 &  1
            P0( 1)=  4.366360000000D-01 (+/- 1.1D-02)     Sensitivity= 3.0D-07
            P0( 2)= -3.529000000000D-03 (+/- 1.3D-04)     Sensitivity= 5.6D-09
            P0( 3)=  1.540000000000D-05 (+/- 6.9D-07)     Sensitivity= 1.0D-10
            Q0( 1)=  4.800000000000D-02 (+/- 2.8D-03)     Sensitivity= 7.1D-07
            Q0( 2)=  1.366000000000D-02 (+/- 2.6D-04)     Sensitivity= 1.4D-08
State 3S  NDE  Bv  function is a  (NP= 7/NQ= 0) Exponential NDE  in  (vD-v)
            P1( 1)=  1.341000000000D-01 (+/- 5.8D-03)     Sensitivity= 5.5D-07
            P1( 2)= -1.686300000000D-02 (+/- 1.1D-03)     Sensitivity= 1.1D-08
            P1( 3)=  9.200000000000D-04 (+/- 8.5D-05)     Sensitivity= 2.2D-10
            P1( 4)= -2.810837000000D-05 (+/- 3.3D-06)     Sensitivity= 4.3D-12
            P1( 5)=  4.924000000000D-07 (+/- 6.9D-08)     Sensitivity= 8.0D-14
            P1( 6)= -4.619520000000D-09 (+/- 7.5D-10)     Sensitivity= 1.5D-15
            P1( 7)=  1.800000000000D-11 (+/- 3.3D-12)     Sensitivity= 2.7D-17

State-2 isotopic Dunham parameters generated from NDE functions:
------------------------------------------------------------------
       we =   93.74407 (  0.04516)
     wexe =    0.45192 (  0.00384)
   T(v= 0)=   36565.89177
 T(v= -1/2)=   36519.13263
 B(v= -1/2)= 1.18327D-01 (  9.9D-04)
   alpha_e = 1.88162D-03 (  4.7D-04)
Re(v= -1/2)=   3.520495 (  0.014678)

==================================================================
 *** Discrepancies for   55 bands/series of Na( 23)-Na( 23) ***
==================================================================
===================================================================
 515 Na( 23)-Na( 23)  {State 3S}--{State X0} Transitions in  55 bands
============================================ Avge. ========
  v'  v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
 ------------------------------------------------------------------
  0   0    4      0     13   2.0D-01   2.0D-01   -1.14157   1.344
  1   0    6      0     15   2.0D-01   2.0D-01    0.16049   0.525
  2   0    8      0     15   2.0D-01   2.0D-01   -0.19121   0.295
.....  Omit 50 lines of analogous output .........................
 56   0    4      0     22   2.0D+00   2.0D+00   -1.02784   1.052
 57   0    1      0     16   2.0D+00   2.0D+00   -0.08259   0.083
-------------- For these   515 lines, overall:  -0.02843   1.029

============================================================
For overall fit to   515 data,  DRMS(deviations)= 1.029
============================================================
```

3. Output for an Analysis of Chemiluminescence (and other) Data for BaO

A truncated copy of the channel-6 output file for the fit to chemiluminescence and other data for BaO yielded by the illustrative input files presented in Sections IV.A and IV.D.1 (see Ref. 52).

```
Input data for  4  isotopomer(s)
*******************************
    Isotopomer      Mass of atom-1    Mass of atom-2      Reduced mass
   --------------    --------------    --------------    --------------
Ba(138)- O( 16)    137.9052420000    15.9949146223     14.3325557307
Ba(137)- O( 16)    136.9058220000    15.9949146223     14.3216898921
Ba(136)- O( 16)    135.9045710000    15.9949146223     14.3106607703
Ba(135)- O( 16)    134.9056840000    15.9949146223     14.2995118465

Use experimental data input file:  BaOband.4

Apply "Sequential Rounding & Refitting" at digit-1 of the (local) parameter
    uncertainty, proceeding sequentially from the LAST parameter to the FIRST.

Fit uses standard  1/[uncertainty(i)]**2  data weighting

State X0 is a Singlet with  Omega= 0
********************  so rotational energies depend on powers of  [J(J+1)- 0]

State A0 is a Singlet with  Omega= 0
********************  so rotational energies depend on powers of  [J(J+1)- 0]

State Ap is a Singlet with  Omega= 0
********************  so rotational energies depend on powers of  [J(J+1)- 0]

Neglect data with:  Uncertainties > UCUTOFF=    9.00     (cm-1)
     and State X0 data with  J > JTRUNC= 200  or  v  outside range  0  to  35
     and State A0 data with  J > JTRUNC= 200  or  v  outside range  0  to   0
     and State Ap data with  J > JTRUNC= 200  or  v  outside range  0  to  99

Absolute zero of energy is fixed at  G(v"=-1/2)  of  State X0
***********************

Fit for State X0  Gv's  uses Dunham expansion of order  5
*********************

Fit for State X0  Bv's  uses Dunham expansion of order  3
*********************

Dunham Fit for State X0  uses  CDC(1)=-Dv  expansion of order  2
=======================        CDC(2)= Hv  expansion of order -1
                               CDC(3)= Lv  expansion of order -1
                               CDC(4)= Mv  expansion of order -1
                               CDC(5)= Nv  expansion of order -1
                               CDC(6)= Ov  expansion of order -1

Use a Band-Constant fit for State A0   Gv's   Bv's  and  CDC's
************************************
     For  v=  0  of  ISOT= 1  fit to the energy and  3 rotational band constants
     For  v=  0  of  ISOT= 2  fit to the energy and  3 rotational band constants
     For  v=  0  of  ISOT= 3  fit to the energy and  2 rotational band constants
     For  v=  0  of  ISOT= 4  fit to the energy and  2 rotational band constants

For State Ap  fit to individual term values for each  {v,J,p,isot}
**********************************
For Ba(138)- O( 16)  fit to 878 T(v,J,p) term values,
                 of which   1 are involved in only one transition
For Ba(137)- O( 16)  fit to 215 T(v,J,p) term values,
                 of which   1 are involved in only one transition
For Ba(136)- O( 16)  fit to 158 T(v,J,p) term values,
                 of which   0 are involved in only one transition
For Ba(135)- O( 16)  fit to 121 T(v,J,p) term values,
                 of which   0 are involved in only one transition

Fit to the origins of    2 fluorescence series with initial-state labels
                 (where  p= 'parity'  &  IS= 'isotope'):
  -------------   -------------   -------------   -------------   -------------
   v'  J'  p IS    v'  J'  p IS    v'  J'  p IS    v'  J'  p IS    v'  J'  p IS
  -------------   -------------   -------------   -------------   -------------
   15  50 +1  1    14  50 +1  1

13683 data fit to 1400 param. yields   DRMS(devn)=  1.207      tst(PS)= 9.0D-03
    PV(   1) =  6.69736610171663D+02 (+/- 6.5D-04)    PS= 5.2D-08   PC= 3.1D-11
    PV(   2) = -2.01953313962454D+00 (+/- 2.1D-01)    PS= 3.9D-09   PC=-2.1D-11
    PV(   3) = -4.16353170235560D-03 (+/- 2.9D-05)    PS= 2.6D-10   PC= 1.7D-12
.......... omit listing of 1394 parameter values from unrounded fit ..........
    PV(1398) =  1.95475346274757D+04 (+/- 8.9D-03)    PS= 3.8D-05   PC=-8.4D-11
    PV(1399) =  3.87781504579061D+04 (+/- 8.2D-01)    PS= 3.5D-03   PC= 1.7D-08
    PV(1400) =  3.84041031910770D+04 (+/- 7.9D-01)    PS= 3.3D-03   PC= 1.4D-08

13683 data fit to   26 param. yields   DRMS(devn)=  1.207      tst(PS)= 5.4D-07
    PV(   1) =  6.69736609987788D+02 (+/- 2.9D-04)    PS= 2.7D-06   PC= 1.3D-13
    PV(   2) = -2.01953325104860D+00 (+/- 1.2D-04)    PS= 2.0D-07   PC=-4.1D-14
    PV(   3) = -4.16350410617215D-03 (+/- 1.9D-05)    PS= 1.3D-08   PC= 6.9D-15
..... omit listing of 1394 parameter vales from fit with rounded term values & FS origins ....
    PV(1398) =  1.95475346000000D+04 (+/- 0.0D+00)    PS= 0.0D+00   PC= 0.0D+00
    PV(1399) =  3.87781500000000D+04 (+/- 0.0D+00)    PS= 0.0D+00   PC= 0.0D+00
    PV(1400) =  3.84041000000000D+04 (+/- 0.0D+00)    PS= 0.0D+00   PC= 0.0D+00

After Sequential Rounding & Refitting,  fit of  1400 parameters to 13683 data
**********************************  yields    DSE=  1.274

State X0  Dunham expansion Gv parameters:
         YLM( 1,0)=  6.697366700000D+02 (+/- 6.5D-04)    Sensitivity= 5.2D-08
```

```
              YLM( 2,0)= -2.019560000000D+00 (+/- 2.1D-04)    Sensitivity= 3.9D-09
              YLM( 3,0)= -4.159400000000D-03 (+/- 2.9D-05)    Sensitivity= 2.6D-10
              YLM( 4,0)= -3.610000000000D-05 (+/- 1.7D-06)    Sensitivity= 1.6D-11
              YLM( 5,0)= -5.400000000000D-07 (+/- 3.6D-08)    Sensitivity= 9.2D-13
State X0  Dunham expansion Bv parameters:
              YLM( 0,1)=  3.126146400000D-01 (+/- 6.3D-08)    Sensitivity= 1.0D-10
              YLM( 1,1)= -1.393745000000D-03 (+/- 8.0D-08)    Sensitivity= 1.8D-11
              YLM( 2,1)= -3.682000000000D-06 (+/- 1.5D-08)    Sensitivity= 1.5D-12
              YLM( 3,1)= -4.590000000000D-08 (+/- 6.8D-10)    Sensitivity= 1.1D-13
State X0  Dunham expansion CDC(1) parameters:
              YLM( 0,2)= -2.714400000000D-07 (+/- 1.2D-10)    Sensitivity= 2.3D-14
              YLM( 1,2)= -1.070000000000D-10 (+/- 1.7D-11)    Sensitivity= 3.1D-15
              YLM( 2,2)= -1.310000000000D-11 (+/- 1.2D-12)    Sensitivity= 2.8D-16

State A0  Pure Band-Constant representation for levels   v= 0 -  0
        Gv(v=  0; 1)=  1.705661700000D+04 (+/- 9.2D-04)    Sensitivity= 1.2D-06
        Bv(v=  0; 1)=  2.578246000000D-01 (+/- 6.1D-07)    Sensitivity= 2.8D-10
       -Dv(v=  0; 1)= -2.781300000000D-07 (+/- 1.8D-10)    Sensitivity= 3.3D-14
        Hv(v=  0; 1)= -1.060000000000D-13 (+/- 7.4D-15)    Sensitivity= 3.2D-18
        Gv(v=  0; 2)=  1.705670590000D+04 (+/- 2.1D-03)    Sensitivity= 2.8D-06
        Bv(v=  0; 2)=  2.580205000000D-01 (+/- 2.8D-06)    Sensitivity= 9.7D-10
       -Dv(v=  0; 2)= -2.783000000000D-07 (+/- 1.0D-09)    Sensitivity= 2.0D-13
        Hv(v=  0; 2)= -1.700000000000D-13 (+/- 1.3D-13)    Sensitivity= 3.5D-17
        Gv(v=  0; 3)=  1.705680080000D+04 (+/- 2.3D-03)    Sensitivity= 3.7D-06
        Bv(v=  0; 3)=  2.582263000000D-01 (+/- 1.9D-06)    Sensitivity= 1.4D-09
       -Dv(v=  0; 3)= -2.810000000000D-07 (+/- 3.4D-10)    Sensitivity= 3.2D-13
        Gv(v=  0; 4)=  1.705689700000D+04 (+/- 2.6D-03)    Sensitivity= 4.5D-06
        Bv(v=  0; 4)=  2.584251000000D-01 (+/- 1.5D-06)    Sensitivity= 1.2D-09
       -Dv(v=  0; 4)= -2.810000000000D-07 (+/- 2.0D-10)    Sensitivity= 1.7D-13


State Ap  1372  fitted term values    Tv{state:v,J,p;isot}
===================================================================
Tv(Ap:  1,  0,+1; 1)=  1.755153390000D+04 (+/- 7.2D-03)    Sensitivity= 3.1D-05
Tv(Ap:  1,  1,+1; 1)=  1.755204970000D+04 (+/- 5.6D-03)    Sensitivity= 2.4D-05
Tv(Ap:  1,  2,+1; 1)=  1.755307330000D+04 (+/- 5.6D-03)    Sensitivity= 2.4D-05
.......... omit listing of 1366 final fitted term values ..........
Tv(Ap:  4, 43,+1; 4)=  1.950282210000D+04 (+/- 7.2D-03)    Sensitivity= 3.1D-05
Tv(Ap:  4, 44,+1; 4)=  1.952493960000D+04 (+/- 7.3D-03)    Sensitivity= 3.1D-05
Tv(Ap:  4, 45,+1; 4)=  1.954753460000D+04 (+/- 8.9D-03)    Sensitivity= 3.8D-05

Energy origins  FS(v', j', p'; isotopomer)  of the    2 fluorescence series
  FS( 15, 50, +1; 1)=  3.877815000000D+04 (+/- 8.2D-01)    Sensitivity= 3.5D-03
  FS( 14, 50, +1; 1)=  3.840410000000D+04 (+/- 7.9D-01)    Sensitivity= 3.3D-03

State-X0 Sensitivity-Rounded YLM's for Minority Isotopomers:
===================================================================
  Ba(137)- O( 16)    Ba(136)- O( 16)    Ba(135)- O( 16)

Zero point level T(v=0) relative to v= -1/2 of the first state considered (X0)
    for the reference isotopomer is:       334.362923
    and for the others:    334.489547     334.618221     334.748445

Semiclassical  Y00  of the reference isotopomer is:  0.020145( 0.000067)
  & of others:  0.020160( 0.000068)  0.020175( 0.000068)  0.020191( 0.000068)

          YLM( 1,0)  6.69990685790D+02 (6.5D-04)   6.70248814530D+02 (6.5D-04)
                     6.70510050620D+02 (6.5D-04)
          YLM( 2,0) -2.02109223600D+00 (2.1D-04)  -2.02264987700D+00 (2.1D-04)
                    -2.02422688000D+00 (2.1D-04)
          YLM( 3,0) -4.16413450000D-03 (2.9D-05)  -4.16894930000D-03 (2.9D-05)
                    -4.17382590000D-03 (2.9D-05)
          YLM( 4,0) -3.61548000000D-05 (1.7D-06)  -3.62105500000D-05 (1.7D-06)
                    -3.62670400000D-05 (1.7D-06)
          YLM( 5,0) -5.41024800000D-07 (3.6D-08)  -5.42067800000D-07 (3.6D-08)
                    -5.43125000000D-07 (3.6D-08)

          YLM( 0,1)  3.12851820100D-01 (6.4D-08)   3.13092932700D-01 (6.4D-08)
                     3.13337042400D-01 (6.4D-08)
          YLM( 1,1) -1.39533145000D-03 (8.1D-08)  -1.39694482000D-03 (8.1D-08)
                    -1.39857887000D-03 (8.1D-08)
          YLM( 2,1) -3.68758900000D-06 (1.5D-08)  -3.69327500000D-06 (1.5D-08)
                    -3.69903700000D-06 (1.5D-08)
          YLM( 3,1) -4.59871000000D-08 (6.8D-10)  -4.60758000000D-08 (6.8D-10)
                    -4.61656000000D-08 (6.8D-10)

          YLM( 0,2) -2.71852040000D-07 (1.2D-10)  -2.72271230000D-07 (1.2D-10)
                    -2.72695960000D-07 (1.2D-10)
          YLM( 1,2) -1.07203000000D-10 (1.7D-11)  -1.07410000000D-10 (1.7D-11)
                    -1.07619000000D-10 (1.7D-11)
          YLM( 2,2) -1.31298000000D-11 (1.2D-12)  -1.31602000000D-11 (1.2D-12)
                    -1.31910000000D-11 (1.3D-12)


===================================================================
  *** Discrepancies for  199 bands/series of Ba(138)- O( 16) ***
===================================================================
===================================================================
  80 State X0 Ba(138)- O( 16) MW transitions in  80 vib. levels
================================================= Avge. ========
  v'  v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
-------------------------------------------------------------------
  0   0    1     49     51   2.1D+00   2.1D+00   -0.79648   0.796
  1   1    1     49     51   5.0D-01   5.0D-01   -2.11159   2.112
  2   2    1     49     51   5.0D-01   5.0D-01   -0.08117   0.081
.......... omit 74 entries for other MW transitions ..........
  0   0    1      7      8   1.0D-06   1.0D-06   -0.02517   0.025
  1   1    1      7      8   1.0D-06   1.0D-06   -3.71707   3.717
```

```
    0    0    1     9    10   1.0D-06  1.0D-06   1.23292   1.233
------------- For these    80 lines, overall:   -0.19677   1.771


===========================================================
 53 State X0 Ba(138)- O( 16) InfraRed transitions in   6 bands
============================================ Avge. ========
  v'   v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
-----------------------------------------------------------
   1    0   12     5    67   5.0D-03  5.0D-03   0.16364   0.231
   2    1   11     0    60   5.0D-03  5.0D-03   0.04330   0.082
   3    2    9     6    70   5.0D-03  5.0D-03   0.03378   0.155
   4    3    5     7    73   5.0D-03  5.0D-03  -0.06224   0.149
   5    4   11     3    67   1.0D-02  1.0D-02  -0.08408   0.105
   6    5    5    10    52   2.5D-02  2.5D-02   0.03271   0.053
------------- For these    53 lines, overall:    0.03154   0.149


===========================================================
 1898 Ba(138)- O( 16)  {State A0}--{State X0} Transitions in  14 bands
============================================ Avge. ========
  v'   v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
-----------------------------------------------------------
   0    0   46     7    62   5.0D-03  5.0D-03  -0.23996   2.177
   0    1   98     7    63   5.0D-03  5.0D-03  -0.09947   1.237
   0    2  112     5    80   5.0D-03  5.0D-03  -0.11029   1.273
   0    3  151     0    91   5.0D-03  5.0D-03  -0.00584   0.887
   0    4  123     3    79   5.0D-03  5.0D-03   0.07406   0.970
   0    2  136     4   105   5.0D-03  5.0D-03  -0.05472   1.359
   0    3  188     3   113   5.0D-03  5.0D-03   0.23293   1.101
   0    4  194     1   116   5.0D-03  5.0D-03   0.09821   0.682
   0    5  191     6   119   5.0D-03  5.0D-03   0.03162   0.810
   0    6  189     3   122   5.0D-03  5.0D-03  -0.00795   1.028
   0    7  170     2   111   5.0D-03  5.0D-03  -0.14477   0.865
   0    8  141     6   101   5.0D-03  5.0D-03  -0.15054   1.021
   0    9  123     8    89   5.0D-03  5.0D-03  -0.21444   1.135
   0   10   36     7    60   5.0D-03  5.0D-03   1.23658   2.764
------------- For these  1898 lines, overall:    0.00386   1.121


===========================================================
 8160 Ba(138)- O( 16)  {State Ap}--{State X0} Transitions in  96 bands
============================================ Avge. ========
  v'   v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
-----------------------------------------------------------
   1    0  145     0    84   5.0D-03  5.0D-03  -0.09782   0.859
   2    0  126     6    88   5.0D-03  5.0D-03  -0.07457   1.108
   3    0  273     0    93   5.0D-03  5.0D-03   0.00248   1.059
   .......... omit 90 entries for other band transitions ..........
  10   19   22     9    28   5.0D-03  5.0D-03   0.06819   1.649
  11   19   44    14    50   5.0D-03  5.0D-03   0.05409   1.249
  11   20   40    10    43   5.0D-03  5.0D-03   0.20866   1.805
------------- For these  8160 lines, overall:    0.00056   1.097


===========================================================
 59 Fluorescence transitions into State X0  Ba(138)- O( 16) in   2 series
============================================ Avge. ===============
  v'   j' p' #data  v"min  v"max  AvgeUnc  Max.Unc.   Err/Unc   DRMSD
-----------------------------------------------------------
  15   50  e   32     0    34   2.5D+00  5.0D+00  -0.06357   1.160
  14   50  e   27     0    33   2.2D+00  5.0D+00  -0.07636   0.586
------------------- For these    59 lines, overall:   -0.06942   0.942


===========================================================
  1 State A0 Ba(138)- O( 16) MW transitions in   1 vib. levels
============================================ Avge. ========
  v'   v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
-----------------------------------------------------------
   0    0    1     2     3   6.7D-05  6.7D-05  -0.28909   0.289
------------- For these     1 lines, overall:   -0.28909   0.289


===========================================================
 *** Discrepancies for   36 bands/series of Ba(137)- O( 16) ***
===========================================================
===========================================================
  6 State X0 Ba(137)- O( 16) MW transitions in   6 vib. levels
============================================ Avge. ========
  v'   v" #data  J"min  J"max  Av.Unc.  Max.Unc.   Err/Unc   DRMSD
-----------------------------------------------------------
   0    0    1     0     1   1.7D-07  1.7D-07  -0.79714   0.797
   0    0    1     1     2   8.3D-07  8.3D-07  -0.30463   0.305
   0    0    1     2     3   6.7D-07  6.7D-07  -0.77455   0.775
   0    0    1     5     6   1.0D-06  1.0D-06  -0.47476   0.475
   0    0    1     7     8   1.0D-06  1.0D-06   0.11551   0.116
   0    0    1     9    10   1.0D-06  1.0D-06   2.25718   2.257
------------- For these     6 lines, overall:    0.00360   1.054

.... omit 176 lines summarizong residual discrepancies for other isotopomers ....


===========================================================
For overall fit to 13683 data,  DRMS(deviations)=  1.207
===========================================================
```