Supplementary Material

This document contains Supplementary Material associated with the paper "**dParFit :** A Computer Program for Fitting Diatomic Molecule Spectral Data to Parameterized Level Energy Expressions", submitted to the *Journal of Quantitative Spectroscopy and Radiative Transfer* in February 2016. It consists of the four Appendices enumerated below. Note that Equation and Reference numbering appearing herein refer to those in the Journal Article. Anyone who wishes to be Registered with the author as a user of this code, eligible to be sent any future bug fixes or updates, should fill in the online form at the www address "http://scienide2.uwaterloo.ca/~rleroy/dParFit16".

Appendix A: Structure and Control Parameters of the Experimental Data 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-state vibrational quantum numbers $v' =$ `VP` and $v'' =$ `VPP`, respectively, by the three-alphanumeric-character labels `LABLP` and `LABLPP` (enclosed between single quotes; e.g. `'X0S'`) 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 'instruction' input file (see Appendix B below).

For each such band, the data are read, one per line, each datum consisting of the upper- and lower-state rotational quantum numbers, $J' =$ `JP` and $J'' =$ `JPP`, respectively, the integer +1 (for e–parity levels) or -1 (for f–parity levels) defining the e/f parity of the upper ($p' =$ `EFP`) and lower ($p'' =$ `EFPP`) level, the experimental datum $y_{\rm obs}(i) =$ `FREQ(i)` and its uncertainty $u(i) =$ `UFREQ(i)`. A datum line with `JP` < 0 signals the end of the data for this band and tells 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 $v' =$ `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 `LABLP` $=$ `'FLS'` identifies the data group as a fluorescence series and causes the 'band' parameters `VP` and `VPP` (see READ #1 above) to be defined as the emitting level vibrational and rotational quantum numbers v' and J', respectively, and the transition labels `JP` and `JPP` (READ #2 above) as the final (lower) state vibrational and rotational quantum numbers v'' and J'', respectively. The parity label parameters `EFP` and `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 `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 that 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 `LABLP` $=$ `'PAS'`. As with fluorescence series, the data parameters `JP`, `JPP` and `EFPP` are defined as the final-state level parameters v'', J'' and parity p'', respectively, while the 'band parameters' `VP` and `VPP` and the data parameter `EFP` are all dummy variables that are ignored by the analysis. Note that **dParFit** expects all PAS data associated with a given isotopologue in a given electronic state to be input as a single 'band'.

The defining property of `PAS`-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 `PAS`-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. [61]). As for fluorescence-series or PAS data, the band-type data structure is retained, but in this case the input parameter value `LABLP` $=$ `'BV'` identifies this data-group as a set of B_v values for electronic state `LABLPP`, and signals that the band parameters `VP` & `VPP` and the transition labels `JPP`, `EFP` & `EFPP` are dummy variables, while input parameter `JP` is actually the vibrational quantum number v, `FREQ` is the B_v value and `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}BaO, ^{137}BaO, ^{136}BaO, ^{135}BaO. In addition to the new electronic chemiluminescence spectra reported in that work,[51] 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  'A1S' 'A1S'   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  'A1S' 'A1S'   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  'A1S' '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
```

Appendix B. Structure and Parameters of the Channel–5 Input ‘Instruction’ Data File

Appendix B.1 Structure of the Channel–5 Input ‘Instruction’ Data File

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,*)  WRITFILE
 #4   READ(5,*)  UCUTOFF, IROUND, ROBUST, LPRINT, PRINP
      DO  ISOT= 1, NISTP
 #5       READ(5,*) MN(1,ISOT), MN(2,ISOT)
          ENDDO
   c***********************************************************************
   c     Begin loop over electronic states
   c***********************************************************************
      DO 60 ISTATE= 1, NSTATES
 #6       READ(5,*) SLABL(ISTATE), IOMEG(ISTATE), JTRUNC(ISTATE), EFSEL(ISTATE),
     1                                                VMIN(ISTATE), VMAX(ISTATE)
 #7       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
 #8                       READ(5,*) IV, (ZK(M,IV,ISTATE,ISOT), M= 0,MMAX)
                        ELSE
 #9                       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
#10       IF(NDEGv(ISTATE).EQ.2) READ(5,*) VS(ISTATE), DVS(ISTATE), IFXVS(ISTATE),
     1                                                              IFXDVS(ISTATE)
          IF((NDEGv(ISTATE).EQ.0).OR.(NDEGv(ISTATE).GE.2)) THEN
#11           READ(5,*) LMAX(0,ISTATE)
              IF(IFXGv(ISTATE).GT.0) THEN
#12               READ(5,*) Te(ISTATE)
#13               READ(5,*) (YLM(L,0,ISTATE), L= 1, LMAX(0,ISTATE))
                  ENDIF
              ENDIF
          IF(NDEGv(ISTATE).GE.1) THEN
#14           READ(5,*) NLR(ISTATE), DLIMIT(ISTATE), vD(ISTATE), Cn(ISTATE), NSIG
#14           READ(5,*) ITYPE(ISTATE), NP0(ISTATE), NQ0(ISTATE), IP0(ISTATE), IQ0(ISTATE)
#16           IF(NP0(ISTATE).GT.0) READ(5,*) (PM0(I,ISTATE),I=1, NP0(ISTATE))
#17           IF(NQ0(ISTATE).GT.0) READ(5,*) (QM0(I,ISTATE),I=1, NQ0(ISTATE))
#18           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
#19                       READ(5,*) IV, (ZK(M,I,ISTATE,ISOT), M= 1,MMAX)
                        ELSE
#20                       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
#21           READ(5,*) LMAX(1,ISTATE)
#22           IF(IFXBv(ISTATE).GT.0) READ(5,*) (YLM(L,1,ISTATE), L= 0, LMAX(1,ISTATE))
              ENDIF
          IF(NDEBv(ISTATE).GE.1) THEN
#23           READ(5,*) ITYPB(ISTATE), NP1(ISTATE), NQ1(ISTATE),
     1                                        IP1(ISTATE), IQ1(ISTATE)
#24           IF(NP1(ISTATE).GT.0) READ(5,*) (PM1(I,ISTATE), I=1,
     1                                                    NP1(ISTATE))
#25           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)
#26                   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)
#27                   READ(5,*,END=200) IV, NRC(IV,ISTATE,ISOT)
                      ENDDO
                  ENDDO
              ENDIF
          IF(NDECDC(ISTATE).EQ.0) THEN
#28           READ(5,*) (LMAX(M,ISTATE),M= 2, NCDC(ISTATE)+1)
              IF(IFXCDC(ISTATE).GT.0) THEN
                  DO  M= 2, NCDC(ISTATE)+1
#29                   READ(5,*) (YLM(L,M,ISTATE),L= 0, LMAX(M,ISTATE))
                      ENDDO
                  ENDIF
          IF(NDECDC(ISTATE).GE.1) THEN
              MMAX= NCDC(ISTATE)+ 1
#30           READ(5,*) (LMAX(M,ISTATE),M= 2, MMAX)
              DO  M= 2,MMAX
#31               READ(5,*)  (RM(I),I= 1, LMAX(M,ISTATE))
                  ENDDO
              ENDIF
       30 IF(IOMEG(ISTATE).NE.0) THEN
#32           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)
#33                           IF(IFXLD(ISTATE).GT.0) READ(5,*) IV,
         1                          (ZQ(MQ0+M,IV,ISTATE,ISOT), M= 1,NLDMX(ISTATE))
#34                           IF(IFXLD(ISTATE).LE.0) READ(5,*) IV, NQC(IV,ISTATE,ISOT)
                              ENDDO
                          ENDDO
                      ENDIF
                  IF(NDELD(ISTATE).GE.0) THEN
#35                   READ(5,*) (LDMAX(MQ0+M,ISTATE),M= 1,NLDMX(ISTATE))
                      IF(IFXBv(ISTATE).GT.0) THEN
```

```
                          DO  M= 1, NLDMX(ISTATE)
#36                           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
#37           IF((IFXGv(ISTATE).LE.0).AND.(ISTATE.EQ.1)) READ(5,*) BOB00
#38           READ(5,*) (LAMAX(1,M,ISTATE), M= 0, BOBORD(ISTATE))
#39           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
#40                        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 in Channel-5 input
   c***********************************************************************
      IF(DATAFILE.EQ.MAKEPRED) THEN
   77     CONTINUE
#41       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***********************************************************************
```

B.1. Definitions of Parameters in the Channel-5 Input 'Instruction' Data File

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`: (±) integer for the total charge on the molecule. It is used to generate the charge-modified reduce mass used for molecular ions,[45] $\mu = M_A\, M_B/(M_A + M_B - m_e \times \texttt{CHARGE})$, 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`′).

#3. `READ(5,*) WRITFILE`

`WRITFILE` is the common root of the names used for the output files written to Channels $6 - 10$, which will have the names `WRITFILE.6`, `WRITFILE.7`, `WRITFILE.8`, ... , `WRITFILE.10`, respectively. `WRITFILE` may consist of up to 40 alphanumeric characters and must be enclosed in single quotes with no leading blanks (e.g., '`EMO4(6,8)u3t1`'). A distinct name should be chosen to identify the results of each particular run, and if the same name is used for subsequent runs, previous files with those names will be over-written.

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.

#4 `READ(5,*) UCUTOFF, IROUND, ROBUST, LPRINT, PRINP`

`UCUTOFF`: neglect any input data with uncertainties $u(i) > \texttt{UCUTOFF}$ (a real number).

`IROUND`: Setting (integer) $\texttt{IROUND} \neq 0$ causes the "sequential rounding and refitting" procedure of Ref. [59] to be implemented, with each parameter being rounded at the |`IROUND`|'th significant digit of its uncertainty. If $\texttt{IROUND} > 0$ the sequential rounding is applied in turn to the remaining free parameter with the largest relative uncertainty; if $\texttt{IROUND} < 0$ the rounding proceeds sequentially from the last parameter to the first. If $\texttt{IROUND} = 0$ 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 `LPRINT` < 0 print converged unrounded parameters; if `LPRINT` ≥ 1 also print converged rounded parameters (when `IROUND` $\neq 0$); if `LPRINT` ≥ 2 also print parameter changes on each rounding step; if `LPRINT` ≥ 3 also report parameter convergence criterion satisfied; if `LPRINT` ≥ 4 also print convergence test on each fitting cycle; if `LPRINT` ≥ 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` $= \alpha = 1$) for parameter mass-scaling and the calculation of BOB corrections. The mass numbers for each isotopologue must be on a different line.

#5 `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 isotopologue $\alpha =$ `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.

#6. `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.

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

`NCDC`: the number of CDCs 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) - (12) for `NDEGv` $= 1$, or d) by the Tellinghuisen-type MXS "mixed" representation of Eq. (14) 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) - (12) if when `NDEBv` $= 1$ (only allowed if `NDEGv` ≥ 1), or d) by the Tellinghuisen-type MXS "mixed" representations of Eq. (15) if `NDEBv` $= 2$ (this option is only allowed if also `NDEGv` $= 2$).

`NDECDC`: as for `NDEGv` and `NDEBv`, specifies whether the CDC s 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. (16) for `NDECDC` $= 0$, or c) by the NDE expressions of Eqs. (8), (9) & (12) for `NDECDC` $= 1$; this last case requires `IFXCDC` $= 1$.

`IFXGv , IFXBv & IFXCDC`: are integers set > 0 if G_v, B_v or the CDC s, respectively, are to be held fixed at values determined by read-in parameters; otherwise (if $\leq$ 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 (#8 − 18) are concerned with the four possible ways of representing G_v for electronic state–s: #8 − 9 govern cases in which band constants are used (`NDEGv` $= -1$), #10 is for MXS functions, #11 − 13 are for Dunham or MXS functions, and #14 − 18 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`$(s) + 1$.

#8. `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 CDC s) *and* are to be determined by the fit (`IFXGv` $\leq$ 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.

#9. `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. (13) 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).

#10. `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`)`

#11. `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.

#12. `READ(5,*) Te(`s`)`

#13. `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.

#14. `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. (11) with $\mathcal{S} = 1$; `ITYPE` $= 2$ when $\mathcal{S} = 2n/(n-2)$, and `ITYPE` $= 3$ when Eq. (12) (with $m = 0$) is used for $\mathcal{F}^{(\alpha)}_0$ in Eq. (7).

- For `ITYPE` $= 1$ or 2, `NPO` $= L + 1 - t$ and `NQO` $= M + 1 - t$ 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. (11).
- For `ITYPE` $= 3$, `NPO` is the numbers of coefficients `PMO`$(i) = p^{(1),0}_i$ in the exponent expansion of Eq. (12) (starting from $i = t$).
- `IPO` $=$ `IQO` $= t$ is the leading power in the numerator and denominator expansions of Eqs. (11) & (12).
- *Note that* if either of `NPO` or `NQO` are ≤ 0, the READ statement for the associated parameters (`PMO` or `QMO`) is omitted. Necessarily `IPO` $=$ `IQO` $= t \geq 1$.

#15. `READ(5,*) ITYPE(`s`), NPO(`s`), NQO(`s`), IPO(`s`), IQO(`s`)`

#16. `READ(5,*) (PMO(I,`s`), I=1, NPO(`s`))`

#17. `READ(5,*) (QMO(I,`s`), I=1, NQO(`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.

#18. `READ(5,*) IFXD(s), IFXvD(s)`

Representation for the inertial rotational constants B_v

Use Read statements #19 − 20 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)`$+1$.

#19. `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.

#20. `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.

#21. `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`$=\alpha=1$.

#22. `READ(5,*) (YLM(L,1,s), L= 0, LMAX(1,s))`

If an NDE function from Eq. (8), (9) and (12) 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 #15-17.

#23. `READ(5,*) ITYPE(s), NP1(s), NQ1(s), IP1(s), IQ1(s)`

#24. `READ(5,*) (PM1(I,s), I=1, NP1(s))`

#25. `READ(5,*) (QM1(I,s), I=1, NQ1(s))`

Representing the centrifugal distortion constants (CDCs)

Read statements #26 − 31 specify how the CDCs for electronic state–s are to be represented. Use Reads #26 − 27 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 #8 or 19), 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.

#26. `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`$=1$.

#27. `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. (16), for each of the `NCDC` rotational orders `M`.

#28. `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.

#29. `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 (12) (only allowed if the CDCs are held fixed, `IFXCDC`>0), read the orders `LMAX(M,`s`)` of the exponent expansions of Eq. (12) 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 #31 is skipped if `LMAX(M,`s`)`≤ 0 for that order `M`.

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

#31. `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.

#32. `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. (17 – 18) or Eqs. (20 – 23)) in the expression be used for Λ–doubling or $^2\Sigma$ splitting for this state. If `NLDMX`≤ 0 ignore such splittings and skip READs #33 – 36.

`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 $(v+1/2)$ 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(MQ0`$+\,m,\ v,\ s,\ \alpha$`)`$=q_m^{(\alpha)}(v)$ for $m=1$ to `NLDMX(`s`)`. `MQ0` is defined internally to specify the rotational order of the leading coefficient for this case.

#33. `READ(5,*) IV, (ZQ(MQ0+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. (17), (20) or (22), 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.

#34. `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. (18) or (21) & (23) for the Λ–doubling or $^2\Sigma$ doubling constants, read the orders of the polynomial in $(v+{}^1\!/\!_2)$ used for each rotational order `LDMAX(MQ0+M,s)`. If a read-in `LDMAX` value is <0, ignore that rotational order.

#35. `READ(5,*) (LDMAX(MQ0+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(MQ0+M,s)` ≥ 0 read the $\{$`QLM(L,`m,s`)` $= q^{(1)}_{l,m}\}$ expansion coefficients of Eq. (18) or the $\{\gamma^{(1)}_{l,m}\}$ coefficients of Eq. (21) & (23). If `NLDMX(s)` or `LDMAX(`m,s`)`<0, ignore the associated READ #35 statement.

#36. `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 $\delta^{A}_{0,0}$ 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.

#37. `READ(5,*) BOB00(s)`

Next, read the orders `LAMAX(atom,M,s)` of the $(v+{}^1\!/\!_2)$ expansions of Eq. (25) for the first atom, $atom=1$. Setting a read-in `LAMAX` value <0 causes that order of corrections to be ignored.

#38. `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 $(v+{}^1\!/\!_2)$ expansions of Eq. (25) for the second atom, $atom=2$. For a homonuclear molecule, skip this READ.

#39. `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`)`$=\delta^{atom}_{l,\mathrm{M}}$ of Eq. (25). 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.

#40. `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.

#41. `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`.

Appendix C Illustrative Cases and Their Their Channel–5 'Instruction' Data Files

This program has been successfully applied to a wide range of cases.[3, 16, 23, 51–53, 56, 59, 61–66] The following subsections briefly describe three of those cases, present the associated Channel–5 instruction data files and (truncated) Channel–6 main output files.

C.1: Combined-Isotopologue Dunham Fit to IR and MW Data for HF and 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. [3]. In order to have the output (see below) 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 0.24 sec of CPU time on a ten-year-old Silicon Graphics workstation.

```
1 9  0  2  1                %  AN(1) AN(2) CHARGE NISTP NSTATES
 'HFDFdata.4'               %  DATAFILE
 'HFDF'                     % WRITEFILE
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)
'XOS' 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
```

Channel-6 output for Dunham fits to IR and MW data for HF and DF

```
Input data for  2  isotopomer(s)
********************************
   Isotopomer     Mass of atom-1   Mass of atom-2    Reduced mass
---------------   --------------   --------------   --------------
 H(  1)- F( 19)     1.0078250322    18.9984031627     0.9570552776
 H(  2)- F( 19)     2.0141017781    18.9984031627     1.8210450253

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 XOS 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 XOS 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 XOS
************************

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

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

Dunham Fit for State XOS  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 X0S  " Gv" BOB corrections for  H  to Dunham expansion of order:  3
                    while IGNORING the constant  delta(0,0)  term
Fit State X0S  " Bv" BOB corrections for  H  to Dunham expansion of order:  2
Fit State X0S  "-Dv" BOB corrections for  H  to Dunham expansion of order:  1
Fit State X0S  " Hv" BOB corrections for  H  to Dunham expansion of order:  1

Full  3-cycle convergence:  {ABS(RMSR/RMSRB)-1}= 4.79D-11  TSTPS= 4.6D-05

  722 data fit to   36 param. yields  DRMS(devn)= 8.5330888D-01  tst(PS)= 4.6D-05
  PV(   1) =  4.13838509021929D+03 (+/- 1.3D-03)    PS= 6.0D-07   PC= -3.1D-12
  PV(   2) = -8.99432415804219D+01 (+/- 1.4D-03)    PS= 2.5D-07   PC=  4.7D-12
  PV(   3) =  9.24504125496127D-01 (+/- 6.1D-04)    PS= 6.3D-08   PC= -2.5D-12
 .................. Omit printout for the next 30 lines ....................
  PV(  34) = -1.25225059010100D-07 (+/- 1.9D-08)    PS= 1.0D-10   PC=  1.5D-17
  PV(  35) = -1.91782064991024D-10 (+/- 1.7D-11)    PS= 1.3D-13   PC=  1.2D-20
  PV(  36) =  5.98435801551054D-11 (+/- 2.0D-11)    PS= 1.4D-13   PC= -1.3D-20
===============================================================================
Round Off  PV(  26)= -6.9506762732614D-20 (+/- 3.84D-20)    PS= 1.06D-23
   fix PV(  26) as  -7.00000000000D-20  & refit:  DRMS(deviations)= 8.53309D-01
Full  2-cycle convergence:  {ABS(RMSR/RMSRB)-1}= 1.15D-11  TSTPS= 6.2D-05
===============================================================================
Round Off  PV(  19)= -5.3915560052793D-11 (+/- 2.09D-11)    PS= 6.25D-15
   fix PV(  19) as  -5.00000000000D-11  & refit:  DRMS(deviations)= 8.53309D-01
Full  2-cycle convergence:  {ABS(RMSR/RMSRB)-1}= 8.66D-11  TSTPS= 1.1D-04
===============================================================================
Round Off  PV(  36)=  6.1128691784786D-11 (+/- 1.86D-11)    PS= 1.53D-13
   fix PV(  36) as   6.00000000000D-11  & refit:  DRMS(deviations)= 8.53393D-01
Full  2-cycle convergence:  {ABS(RMSR/RMSRB)-1}= 1.53D-10  TSTPS= 3.8D-06
===============================================================================
 .......... omit printout for the next 30 rounding steps ...................
Full  2-cycle convergence:  {ABS(RMSR/RMSRB)-1}= 3.30D-11  TSTPS= 3.6D-08
===============================================================================
Round Off  PV(   2)= -8.9943188748373D+01 (+/- 1.26D-05)    PS= 2.92D-06
   fix PV(   2) as  -8.99431900000D+01  & refit:  DRMS(deviations)= 8.54599D-01
Full  2-cycle convergence:  {ABS(RMSR/RMSRB)-1}= 1.05D-10  TSTPS= 2.1D-08
===============================================================================
Round Off  PV(   6)=  2.0953712028941D+01 (+/- 4.72D-07)    PS= 3.22D-07
   fix PV(   6) as   2.09537120000D+01  & refit:  DRMS(deviations)= 8.54622D-01
Full  2-cycle convergence:  {ABS(RMSR/RMSRB)-1}= 0.00D+00  TSTPS= 8.7D-09
===============================================================================
Round Off  PV(   1)=  4.1383850252678D+03 (+/- 1.54D-05)    PS= 2.10D-05
   fix PV(   1) as   4.13838503000D+03  & refit:  DRMS(deviations)= 8.54630D-01

  722 data fit to   36 param. yields  DRMS(devn)= 8.5484678D-01
  PV(   1) =  4.13838503000000D+03 (+/- 1.4D-03)    PS= 6.0D-07   PC=  6.0D-05
  PV(   2) = -8.99431900000000D+01 (+/- 1.4D-03)    PS= 2.5D-07   PC= -5.2D-05
  PV(   3) =  9.24488000000000D-01 (+/- 6.1D-04)    PS= 6.3D-08   PC=  1.6D-05
 .................. Omit printout for the next 30 lines ....................
  PV(  34) = -1.26000000000000D-07 (+/- 1.9D-08)    PS= 1.0D-10   PC=  7.7D-10
  PV(  35) = -1.90000000000000D-10 (+/- 1.7D-11)    PS= 1.3D-13   PC= -1.8D-12
  PV(  36) =  6.00000000000000D-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= 0.8770

State X0S  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 X0S  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 X0S  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 X0S  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 X0S  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 X0S  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 X0S  Dunham expansion CDC(5) parameters:
           YLM( 0,6)= -7.000000000000D-20 (+/- 3.8D-20)    Sensitivity= 1.1D-23
State X0S  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-X0S Sensitivity-Rounded parameters's for Minority Isotopomers:
================================================================
    H(  2)- F( 19)

Zero point level T(v=0) relative to v= -1/2 of the first state considered (X0S)
   for the reference isotopomer is:    2046.821296
   and for the others:   1488.266832

Semiclassical  Y00  of the reference isotopomer is:  3.947346( 0.000393)
   & of others:  2.072828( 0.000077)

          YLM( 1,0)  3.00008176870D+03 (7.6D-04)
          YLM( 2,0) -4.72711540000D+01 (6.7D-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 (1.4D-06)
          YLM( 1,1) -3.02202795000D-01 (4.1D-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 (7.0D-09)
          YLM( 1,2)  1.17046500000D-05 (6.4D-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 (6.2D-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 X0S  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 X0S  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 X0S  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   -0.04725   0.780
  1   1    38     10     44   5.4D-04  1.0D-03   -0.22576   0.944
  2   2    21     11     39   7.0D-04  2.0D-03   -0.26451   0.878
  3   3     6     27     33   1.0D-03  1.0D-03   -0.54273   0.924
-------------- For these   115 lines, overall:   -0.17176   0.863

===============================================================
 281 State X0S  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   -0.02010   0.630
  2   1    85      0     30   6.7D-04  2.0D-03    0.09020   0.830
  3   2    59      0     24   6.4D-04  2.0D-03   -0.05247   0.795
  4   3    32      0     22   5.9D-04  2.0D-03   -0.03148   0.680
  5   4    16      2     18   5.0D-04  5.0D-04    0.14964   1.033
-------------- For these   281 lines, overall:    0.01484   0.762

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

C.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 at read-in values taken from the literature: `IFXGv(1)` = `IFXBv(1)` = `IFXCDC(1)` = 1 .

The term values for the upper ($s = 2$) 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 CDC s were held fixed at numerically calculated read-in band-constant values, so this data file had to include a full listing of those CDC s. The values of these CDC s were generated separately (using program LEVEL [33]) from an RKR potential calculated [30] from the pure NDE G_v and B_v expressions yielded by the iterative self-consistent procedure described in Section 2.3.2. 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 0.20 sec of CPU time on a ten-year-old Silicon Graphics workstation.

```
 11 11  0  1 2           %  AN(1) AN(2) CHARGE NISTP NSTATES
 'Na2.4'                 %  DATAFILE
 'Na2_NDE-fit'
 90.d0  1  0  -1  0      %  UCUTOFF IROUND ROBUST LPRINT PRINP
 23  23                  %  MN(1,ISOT=1)  MN(2,ISOT=1)
 'X0S' 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}
 '3Sig' 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
```

Channel–6 Output for NDE Fit to PFOODR Data for the $1^3\Sigma_g^-$ *State of* Na_2

Note that immediately following the listing of the final rounded NDE expansion parameters, the output presents the implied values [55] of the ‘conventional’ molecular constants: ω_e , $\omega_e x_e$, $B_e \equiv B_{v=-1/2}$, and α_e , and their uncertainties.

```
Input data for  1  isotopomer(s)
********************************
   Isotopomer      Mass of atom-1   Mass of atom-2    Reduced mass
---------------    --------------   --------------   --------------
Na( 23)-Na( 23)     22.9897692820    22.9897692820    11.4948846410

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 X1S is a Singlet with  Omega= 0
*********************  so rotational energies depend on powers of  [J(J+1)- 0]

Fixed State X1S  Gv for Isot.-1 defined relative to  T(v=-1/2)=     0.00000 cm-1
Fixed State X1S  Gv  values defined by isotopomer-1 Dunham coefficients:
 0.000000000000D+00
Fixed State X1S  Bv  values defined by isotopomer-1 Dunham coefficients:
 0.000000000000D+00

State X1S  Constants for  Na( 23)-Na( 23)  held fixed at values:
  v       Gv          Bv
 --------------------------
  0     0.00000  0.00000000

State 3Sg 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 3Sg 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
                1.6000000000000D-05
    Input denominator coefficients:  4.9700000000000D-02  1.4000000000000D-02

State 3Sg 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 3Sg  CDC’s  at read-in values

State 3Sg  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
  3 -7.13809D-07  6.20389D-12 -1.22458D-16 -8.74113D-22
 .......................................................
 ..... Omit listing input CDCs for next 50 levels ....
 .......................................................
 54 -2.69835D-06 -2.21373D-10 -4.34372D-14 -1.19404D-17
```

```
 55 -3.08187D-06 -3.25742D-10 -8.52296D-14 -3.12703D-17
 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 X1 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 3Sg  Gv's to NDE or MXS function while fixing   DLIMIT= 39951.59100
*******************************************
State 3Sg  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 3Sg  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)= 1.0290027D+00  tst(PS)= 2.1D-01
  PV(   1) =  4.38613433878127D-01 (+/- 1.1D-02)    PS= 3.0D-07   PC= -1.1D-08
  PV(   2) = -3.55168069235371D-03 (+/- 1.3D-04)    PS= 5.6D-09   PC=  1.1D-10
  PV(   3) =  1.55234937541347D-05 (+/- 7.0D-07)    PS= 1.0D-10   PC= -5.7D-13
  PV(   4) =  4.85049338685694D-02 (+/- 2.8D-03)    PS= 7.2D-07   PC= -2.4D-09
  PV(   5) =  1.37042062768564D-02 (+/- 2.6D-04)    PS= 1.4D-08   PC= -2.8D-10
  PV(   6) =  1.34927181950687D-01 (+/- 5.8D-03)    PS= 5.5D-07   PC= -1.3D-09
  PV(   7) = -1.70156484796423D-02 (+/- 1.1D-03)    PS= 1.1D-08   PC= -4.7D-11
  PV(   8) =  9.31322135942200D-04 (+/- 8.5D-05)    PS= 2.2D-10   PC=  1.4D-11
  PV(   9) = -2.85420664705472D-05 (+/- 3.3D-06)    PS= 4.3D-12   PC= -7.4D-13
  PV(  10) =  5.01480767751510D-07 (+/- 6.9D-08)    PS= 8.0D-14   PC=  1.7D-14
  PV(  11) = -4.71831215949320D-09 (+/- 7.5D-10)    PS= 1.5D-15   PC= -1.7D-16
  PV(  12) =  1.84371050131117D-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 3Sg  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 3Sg  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 3Sg}--{State X1S} 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 similar 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
============================================================
```

C.3: Dunham and Band Constant Fit to MW, IR, Fluorescence and Chemiluminescence data for 3 Isotopologues of BaO

The final illustrative case considered here is a fit to microwave, infrared, 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. [51]). A fragment of the 16 537-line experimental data file for this case was presented at the end of Appendix A. For this case, the most abundant isotopologue ^{138}Ba^{16}O was chosen as the reference species ($\alpha = 1$) [51], so its mass numbers are read first. For the ground $X\,^1\Sigma^+$ electronic state (′`X1S`′) the term values were represented by Dunham expansions for all of G_v & B_v and the CDC s. Unperturbed levels associated with $v' = 0$ in the excited $A\,^1\Sigma^+$ state (′`A1S`′) 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,[51] 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 `A1S`, 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 `A1p`, for which state one reads in `NDEGv` $= -2$. In other words, although only two electronic states are directly involved in the chemiluminescence spectrum, we set `NSTATES` $= 3$, and treat bands involving A-state levels $v' \geq 1$ as if they actually belonged to a different electronic state, `A1p`.

The resulting fit to 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. [51]. This fit required 20.1 min of CPU time on a 10-year-old Silicon Graphics workstation. 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. [63] required only 0.40 sec of CPU time. Moreover, if the same BaO fit is done with no rounding, the CPU time drops by a more than factor of four; 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 modest set of 26 Dunham-type and band-constant parameters. The Channel–5 'Instruction' input file for this analysis is listed below, followed by a compressed version of the resulting main Channel–6 output file.

```
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)
'X1S' 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), ...
'A1S' 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
'A1p' 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
```

Channel-6 output for Dunham and Band Constant Fit to data for 4 Isotopologues of BaO

A truncated copy of the Channel-6 output file for the fit to chemiluminescence and other data for BaO described above (see Ref. [51]).

```
Input data for  4  isotopomer(s)
********************************
   Isotopomer      Mass of atom-1   Mass of atom-2    Reduced mass
---------------    --------------   --------------   --------------
Ba(138)- O( 16)    137.9052470000    15.9949146196    14.3325557825
Ba(137)- O( 16)    136.9058271000    15.9949146196    14.3216899458
Ba(136)- O( 16)    135.9045757300    15.9949146196    14.3106608206
Ba(135)- O( 16)    134.9056883800    15.9949146196    14.2995118935

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 X1S is a Singlet with  Omega= 0
*********************  so rotational energies depend on powers of  [J(J+1)- 0]

State A1S is a Singlet with  Omega= 0
*********************  so rotational energies depend on powers of  [J(J+1)- 0]

State A1p 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 X1S data with  J > JTRUNC= 200  or  v  outside range  0  to  35
      and State A1S data with  J > JTRUNC= 200  or  v  outside range  0  to   0
      and State A1p 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 X1
************************

Fit for State X1S  Gv's  uses Dunham expansion of order  5
*********************

Fit for State X1S  Bv's  uses Dunham expansion of order  3
*********************

Dunham Fit for State X1S  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 A1S   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 A1p  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)= 1.2068264D+00  tst(PS)= 6.2D-05
  PV(   1) =  6.69736610181026D+02 (+/- 6.5D-04)    PS= 5.2D-08   PC=  3.0D-13
  PV(   2) = -2.01953314827863D+00 (+/- 2.1D-04)    PS= 3.9D-09   PC= -1.3D-13
  PV(   3) = -4.16353034024503D-03 (+/- 2.9D-05)    PS= 2.6D-10   PC=  1.6D-14
 ...... omit the listing of 1394 unrounded parameters from the initial fit ....
  PV(1398) =  1.95475346289899D+04 (+/- 8.9D-03)    PS= 3.8D-05   PC= -2.3D-13
  PV(1399) =  3.87781504591244D+04 (+/- 8.2D-01)    PS= 3.5D-03   PC=  1.9D-12
  PV(1400) =  3.84041031919821D+04 (+/- 7.9D-01)    PS= 3.3D-03   PC=  2.8D-12

13683 data fit to   25 param. yields  DRMS(devn)= 1.2068370D+00  tst(PS)= 1.1D-06
  PV(   1) =  6.69736610000000D+02 (+/- 0.0D+00)    PS= 0.0D+00   PC=  0.0D+00
  PV(   2) = -2.01953327971380D+00 (+/- 4.9D-05)    PS= 2.1D-07   PC= -3.8D-14
  PV(   3) = -4.16349714166604D-03 (+/- 1.1D-05)    PS= 1.4D-08   PC=  1.1D-14
 ........ omit the listing of 1394 Rounded parameters from the final fit .....
  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 X1S  Dunham expansion Gv parameters:
           YLM( 1,0)=  6.697366100000D+02 (+/- 6.5D-04)    Sensitivity= 5.2D-08
           YLM( 2,0)= -2.019542400000D+00 (+/- 2.1D-04)    Sensitivity= 3.9D-09
           YLM( 3,0)= -4.160900000000D-03 (+/- 2.9D-05)    Sensitivity= 2.6D-10
           YLM( 4,0)= -3.606000000000D-05 (+/- 1.7D-06)    Sensitivity= 1.6D-11
           YLM( 5,0)= -5.400000000000D-07 (+/- 3.6D-08)    Sensitivity= 9.2D-13
State X1S  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 X1S  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 A1S  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 (+/- 1.0D-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 A1p  1372  fitted term values   Tv{state:v,J,p;isot}
====================================
Tv(A1:  1,  0,+1; 1)=  1.755153390000D+04 (+/- 7.2D-03)    Sensitivity= 3.1D-05
Tv(A1:  1,  1,+1; 1)=  1.755204970000D+04 (+/- 5.6D-03)    Sensitivity= 2.4D-05
Tv(A1:  1,  2,+1; 1)=  1.755307330000D+04 (+/- 5.6D-03)    Sensitivity= 2.4D-05
............. Omit the listing of 1366 final fitted term values .............
Tv(A1:  4, 43,+1; 4)=  1.950282210000D+04 (+/- 7.2D-03)    Sensitivity= 3.1D-05
Tv(A1:  4, 44,+1; 4)=  1.952493960000D+04 (+/- 7.3D-03)    Sensitivity= 3.1D-05
Tv(A1:  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-X1S Sensitivity-Rounded parameters'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 (X1)
   for the reference isotopomer is:     334.362897
   and for the others:    334.489521    334.618196    334.748419

Semiclassical  Y00  of the reference isotopomer is:  0.020149( 0.000077)
   & of others:  0.020164( 0.000077)  0.020180( 0.000077)  0.020196( 0.000078)

          YLM( 1,0)  6.69990625720D+02 (6.5D-04)  6.70248754520D+02 (6.5D-04)
                     6.70509990660D+02 (6.5D-04)
          YLM( 2,0) -2.02107462300D+00 (2.1D-04) -2.02263225100D+00 (2.1D-04)
                    -2.02420924000D+00 (2.1D-04)
          YLM( 3,0) -4.16563620000D-03 (2.9D-05) -4.17045280000D-03 (2.9D-05)
                    -4.17533110000D-03 (2.9D-05)
          YLM( 4,0) -3.61147400000D-05 (1.7D-06) -3.61704300000D-05 (1.7D-06)
                    -3.62268500000D-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)  3.13092932800D-01 (6.4D-08)
```

```
                     3.13337042500D-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 X1S 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 X1S 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    0.15775   0.227
  2   1    11      0     60   5.0D-03  5.0D-03    0.04197   0.082
  3   2     9      6     70   5.0D-03  5.0D-03    0.03561   0.155
  4   3     5      7     73   5.0D-03  5.0D-03   -0.05847   0.148
  5   4    11      3     67   1.0D-02  1.0D-02   -0.08174   0.103
  6   5     5     10     52   2.5D-02  2.5D-02    0.03365   0.053
-------------- For these    53 lines, overall:    0.03117   0.147

=======================================================================
 1898 Ba(138)- O( 16)  {State A1S}--{State X1S} 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   -0.23480   2.177
  0   1    98      7     63   5.0D-03  5.0D-03   -0.08842   1.236
  0   2   112      5     80   5.0D-03  5.0D-03   -0.09791   1.272
  0   3   151      0     91   5.0D-03  5.0D-03    0.00470   0.887
  0   4   123      3     79   5.0D-03  5.0D-03    0.08084   0.971
  0   2   136      4    105   5.0D-03  5.0D-03   -0.04235   1.359
  0   3   188      3    113   5.0D-03  5.0D-03    0.24348   1.103
  0   4   194      1    116   5.0D-03  5.0D-03    0.10498   0.683
  0   5   191      6    119   5.0D-03  5.0D-03    0.03373   0.810
  0   6   189      3    122   5.0D-03  5.0D-03   -0.01056   1.028
  0   7   170      2    111   5.0D-03  5.0D-03   -0.15152   0.866
  0   8   141      6    101   5.0D-03  5.0D-03   -0.16038   1.023
  0   9   123      8     89   5.0D-03  5.0D-03   -0.22606   1.137
  0  10    36      7     60   5.0D-03  5.0D-03    1.22454   2.759
-------------- For these  1898 lines, overall:    0.00683   1.121

=======================================================================
 8160 Ba(138)- O( 16)  {State A1p}--{State X1S} 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   -0.09266   0.858
  2   0   126      6     88   5.0D-03  5.0D-03   -0.06941   1.107
  3   0   273      0     93   5.0D-03  5.0D-03    0.00763   1.059
 .......... omit 90 entries for other bands ....................
 10  19    22      9     28   5.0D-03  5.0D-03    0.03145   1.648
 11  19    44     14     50   5.0D-03  5.0D-03    0.01736   1.248
 11  20    40     10     43   5.0D-03  5.0D-03    0.14704   1.798
-------------- For these  8160 lines, overall:   -0.00082   1.097

===========================================================================
  59 Fluorescence transitions into State X1S  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   -0.06463   1.158
 14  50  e    27      0     33   2.2D+00  5.0D+00   -0.07744   0.585
----------------- For these    59 lines, overall:   -0.07049   0.940

===============================================================
   1 State A1S 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 X1S 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   -0.79762   0.798
  0   0     1      1      2   8.3D-07  8.3D-07   -0.30482   0.305
  0   0     1      2      3   6.7D-07  6.7D-07   -0.77491   0.775
  0   0     1      5      6   1.0D-06  1.0D-06   -0.47524   0.475
  0   0     1      7      8   1.0D-06  1.0D-06    0.11487   0.115
  0   0     1      9     10   1.0D-06  1.0D-06    2.25638   2.256
-------------- For these     6 lines, overall:    0.00311   1.054
........................................................................
... omit 176 lines summarizing discrepancies for other isotopologues ...
........................................................................
==========================================================
For overall fit to 13683 data,  DRMS(deviations)=  1.207
============================================================
```

Appendix F. 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 `IROUND` $\neq 0$) the "sequential rounding and refitting" procedure of Ref. [59]).
    - `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.[59]
  - `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.