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~~NCU~~

SPECTRO
a theoretical spectroscopy package

Version 3.0

Cambridge, January 1994.

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SPECTRO

Version 3.0

1.1 Introduction

The prediction of spectroscopic observables from ab initio data can be used in two distinct ways. The first is to compare the results of such a calculation with experimental results in order to verify the accuracy of the optimised geometry and force field. The second is to predict the spectroscopic constants of a molecule which is experimentally unobserved. A computer is the obvious tool to use to generate the large number of constants. The theoretical predictions can then be used by the experimentalist to locate and identify vibrational and rotational transitions.

SPECTRO uses the geometry and force field of any molecule. Changing to a normal coordinate system it performs a rotational analysis, calculating rotational constants, quartic and sextic centrifugal distortion constants and rotation-vibration interaction constants. It then performs a vibrational analysis finding anharmonic constants and fundamental frequencies. The effects of Fermi and Coriolis resonance can be accounted for. It can also be used to generate vibrational transition intensities, given the molecule's dipole moment field. It calculates these intensities using the same perturbation theory approach used in the derivation of the spectroscopic constants.

1.2 Attribution

All published work using this program should reference:

J.F. Gaw, A. Willetts, W.H. Green and N.C. Handy, in "Advances in Molecular Vibrations and Collision Dynamics", ed. J. M. Bowman, JAI Press, Greenwich, CT (1990).

Papers citing intensities generated using this program should also reference:

A. Willetts, N.C. Handy, W.H. Green, and D. Jayatilaka, *J. Phys. Chem.* **94**, 5608 (1990).

Other references which may be helpful include:

W.H. Green, D. Jayatilaka, A. Willetts, R.D. Amos, and N.C. Handy, *J. Chem. Phys.* **93**, 4965 (1990).

W.H. Green, A. Willetts, D. Jayatilaka, and N.C. Handy, *Chem. Phys. Lett.* **169**, 127 (1990).

T.J. Lee, A. Willetts, J.F. Gaw and N.C. Handy, *J. Chem. Phys.* **90**, 4330 (1989).

E.D. Simandiras, J.F. Gaw and N.C. Handy, *Chem. Phys. Lett.* **141**, 166 (1987).

R.D. Amos, J.F. Gaw, N.C. Handy and S. Carter, *J. Chem. Soc. Far. II*, **84**, 1247 (1988).

J.F. Gaw, P. Palmieri, A. Degli Esposti and N.C. Handy, *J. Chem. Phys.* **89**, 959 (1988).

N.C. Handy, J.F. Gaw and E.D. Simandiras, *J. Chem. Soc. Far. II*, **83**, 1577 (1987).

J.F. Gaw and N.C. Handy, *Chem. Phys. Lett.* **128**, 182 (1986).

J.F. Gaw, Y. Yamaguchi, H.F. Schaefer and N.C. Handy, *J. Chem. Phys.* **85**, 5132 (1986).

J.F. Gaw and N.C. Handy, *Chem. Phys. Lett.* **121**, 321 (1985).

The authors intend that this program will eventually be made widely available. However, until the program is ready for wide distribution, please do not distribute this program to others

without our permission. Others who are interested in obtaining copies of the program should apply to us personally. We will endeavour to keep all of the users informed of revisions and updates.

1.3 Acknowledgements

We are grateful for discussions and for the use of data for comparisons with the work of many distinguished scientists. In particular we acknowledge Dr. Roger D. Amos, Professor J. E. Boggs, Dr. Stuart Carter, Dr. Timothy J. Lee, Professor Paolo Palmieri, Dr. E.D. Simandiras, Dr. W. Thiel, and Dr. Y. Yamaguchi. We are especially grateful to Ming-Der Su for help in the programming, and to Professor Ian M. Mills for many fruitful discussions. We also wish to thank the SPECTRO users whose helpful feedback has led to many improvements in the program. We also acknowledge Dr. M. E. Mura for help with the typesetting of this document.

1.4 Cautions and Comments

SPECTRO is written in standard Fortran, without the use of TAB characters or specialized features. It should compile on most systems without difficulty.

The program has been tested on a variety of systems, and is believed to be correct for most uses. A few failures in specialized applications have been noted, and are listed below; work is in progress on correcting these deficiencies. By far, the most common sources of error are mistakes in the input data; the authors recommend that this data be checked several times before concluding that there is a bug in the code. The program prints messages in the output that will hopefully lead to the discovery of these problems. One common problem to watch for is the confusion of restricted and unrestricted summation coefficients; others are unit problems and inconsistent labelling of the vibrational modes. Some errors can be detected by checking that the Coriolis constants satisfy their symmetry relations. We have tried to make all of the input free format. The program's memory is dynamically allocated; for very large molecules there may be array dimensions which need to be increased. Please contact us for special help with these cases. **If you are convinced you have found a bug, please let us know.**

Many of the options are designed for debugging, or for very specialized uses; the user will be well advised to avoid changing the more obscure options until he or she is satisfied with the standard output. The spherical top codes (see Appendix L) are more difficult to use and less tested than the asymmetric and symmetric top codes; users are advised to consult the authors with any problems.

In cases of resonances involving more than two states, the user must do the required diagonalizations by hand. SPECTRO will remove the near-singular terms properly from the spectroscopic constants.

The intensity code is very new and has not been completely tested; we are confident that it works for small symmetric and asymmetric tops, but we have not yet tried to apply it to large molecules nor to spherical top molecules. The intensity code removes resonance denominators without waiting for a directive from the user; the denominators removed are noted in the output.

If the input is started from internal coordinates, the Cartesian fields generated are adequate for the calculations that follow, but are not, strictly speaking, exact. The way we have done this makes these Cartesian fields not isotope-independent. We recommend that the user do a different SPECTRO run starting from the internal field for each isotopic species desired.

The program removes the Darling-Dennison resonance terms, but does not construct the 2x2 resultant matrix. Also, the program cannot yet handle restricted-summation dipole fields. The treatment of spherical tops is not as complete nor as user-friendly as for other types of molecules. Work is in progress.

1.5 Overview of the SPECTRO manual

Many spectroscopic constants are calculated by SPECTRO, in particular:

- (1) anharmonic constants;
- (2) Coriolis coupling constants;
- (3) quartic and sextic centrifugal distortion constants;
- (4) vibration-rotation interaction constants;
- (5) vibrational transition intensities.

The program has been tested against other calculations for these constants. They are evaluated for both asymmetric top molecules and symmetric top molecules, and many constants are also calculated for spherical top molecules. Some of the theoretical background is given in the Appendices, and the structure of the commands and data fields to run SPECTRO are given in Sections 1.6-1.24.

To compute these spectroscopic constants, SPECTRO needs a geometry and a force field. If intensities are desired, one must also provide a linear, quadratic, or cubic dipole field. The force field can be quadratic, cubic or quartic, and both the geometry and the fields can be expressed in a variety of coordinate systems using various units and conventions. The different coordinate systems SPECTRO can handle are discussed in Appendices E-G. Whatever the initial input, SPECTRO transforms the geometry and the fields to the principal-axis, dimensionless normal coordinate system used in the perturbation theory calculations, and then, if desired, transforms the fields back to a specified coordinate system. The user must tell the program exactly which type of fields are being provided, using the main input, Section 1.6, and must also specify the equilibrium geometry, Section 1.7.

Because there are so many different spectroscopic constants, transformed force fields, and other quantities of interest to particular users, SPECTRO generates a very large amount of output - larger than most users like to handle. Commands to control and restrict this output are discussed in Sections 1.6 and 1.12.

Different formulae are used if the molecule is an asymmetric top, a symmetric top, or a spherical top as discussed in Appendices. If the molecule is a symmetric top or spherical top, additional information regarding the alignment and labelling of degenerate modes must be provided by the user, as described in Sections 1.8, 1.22 and 1.23.

The most common failure of the perturbation approach occurs when there is a Fermi, Coriolis, or Darling-Dennison resonance. When this occurs, terms involving the resonance denominator should be removed from the perturbation sum, and a matrix should be diagonalized to treat the resonant interaction more exactly. The theory is discussed in Appendices H and

I; the necessary inputs for telling SPECTRO which interactions are resonant are detailed in Section 1.14.

There are a number of specialized instructions recognized by SPECTRO, ranging from simple things like changing isotopes, Section 1.10, to rather esoteric calculations and debugging options.

The constants that one will see after running SPECTRO are detailed below. The output is clearly labelled to aid identification. Obviously if one runs with a quadratic field only, then those constants dependent upon a cubic or quartic field are not calculated; similarly if one includes the cubic field but omits the quartic field a few more constants are generated. Users should note that anharmonic corrections to the vibrational transition intensities require both a quartic force field and a cubic dipole field, since both mechanical and electrical anharmonicity contribute to the effect.

The authors will be pleased to hear from users concerning errors, suggestions for improvement in style, or proposals for the evaluation of further constants of interest.

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Input Specification

1.6 The Main SPECTRO Input.

1.6.1 Program control.

◇ The Keyword Input.

Uses FORTRAN unit 7. The current keywords are listed below. Each word should be uppercase, separated by spaces from other words. Subsidiary information is read, within one or two words of the keyword, to the left and then to the right. Any number of complete sentences, each ending with a '.', may be typed on a line, but only one keyword should appear in each sentence. (Commas have the same effect as periods.) Sentences should not run from one line to the next. Blank lines are permitted. The keyword END terminates the input. Any input not corresponding to a keyword or its subsidiary modifiers is ignored by the program. This is useful for inserting comments in the input.

◇ Integer Input.

Uses FORTRAN unit 5. Input is in the form of 29 integers, 1-15 on the first line, in free format, under SPECTRO.

These input methods are entirely equivalent. All input in the data file, FORTRAN unit 5, is read under a banner of the form # INPUT ##, where INPUT indicates the type of data which follows.

◇ Example: to calculate the spectroscopic constants of ammonia from a quartic Cartesian force field taking into account one 2:1 Fermi resonance, and to convert the force field to internal coordinates, one could use the following:

⊙ Format.

```
INPUT FOR AMMONIA. RUN CARTESIAN TO NORMAL TO INTERNAL.  
READ ENERGY DERIVATIVE DEGREE FOUR.  
INPUTTING A CARTESIAN GEOMETRY.  
THERE IS ONE FERMI TYPE 1 RESONANCE.  
THERE ARE 3 STRETCHES. 2 BENDS. AND 1 OUT OF PLANE BEND.  
END OF INPUT.
```

An equivalent Integer Input in file 5 is:

```
# SPECTRO ##  
0 0 3 2 0 1 0 4 0 0 0 0 0 0 0  
0 1 0 0 0 0 0 0 0 0 0 0 0 0 0
```

In both cases, the program instructions are echoed at the top of the output file to allow easy verification.

◇ Keywords.

The overall “direction” of the program must be specified with a keyword phrase containing one of the following elements:

CARTESIAN NORMAL INTERNAL

CARTESIAN NORMAL

INTERNAL NORMAL

INTERNAL CARTESIAN

The first keyword in the phrase specifies whether the input fields will be in cartesian or internal coordinates. Subsequent keywords specify the coordinate transformations to be used. The order of these keywords is important. For example, the first phrase means “read Cartesian input, convert to normal coordinates and then to internal coordinates” (the same as setting $N_{cart}=0$). All of the other keywords follow a simpler grammar: one keyword in each sentence, with its subsidiary words nearby (in any order). The current keywords are:

◇ Keyword - GEOMETRY

◇ Subsidiary - CARTESIAN, INTERNAL, TAPE

◇ Description - tells the program where to find the geometry.

Always required. See Sec. 1.7 and Igeom.

◇ Keyword - ISOTOPE, ISOTOPES

◇ Description - used to make an isotopic change.

Optional. See Sec. 1.10 and Isotop.

◇ Keyword - DERIVATIVE

◇ Subsidiary - ENERGY, DIPOLE, POLARISABILITY, HYPERPOLARISABILITY [NUMBER]

◇ Alternative - POLARIZABILITY, HYPERPOLARIZABILITY

◇ Description - the degree of energy, dipole, polarisability or hyperpolarisability derivative.

ENERGY DERIVATIVE is always required, all other derivatives are optional.

See Sec. 1.9, Sec. 1.17, N_{deriv} , N_{prop} .

◇ Keyword - CONVERT

◇ Description - changes the units and coordinate systems of the polarisabilities and hyperpolarisabilities.

This is in preparation for the calculation of the vibrational contributions to (hyper) polarisabilities.

- ◇ Keyword - FINITE
- ◇ Description - calculates the new geometry and potential in the presence of an electric field.
Currently used in the calculation of the vibrational contributions to (hyper) polarisabilities.
- ◇ Keyword - POLAR
- ◇ Description - calculates the vibrational contributions to (hyper) polarisabilities using analytic formulae derived from perturbation theory.
- ◇ Keyword - RAMAN
- ◇ Description - calculates properties of the Raman spectrum.
- ◇ Keyword - PUNCH
- ◇ Description - read the quadratic Cartesian force field in HONDO format.
Optional. See Sec. 1.9. (This corresponds to negative Nderiv).
- ◇ Keywords - STRETCH, BEND, LINEAR, PLANE, TORSION
- ◇ Alternate Keywords - STRETCHES, BENDS, TORSIONS
- ◇ Subsidiary - [NUMBER]
- ◇ Description - the number of each type of internal coordinate.
Required if you are using internal coordinates in the input, or if you would like an internal field in the output. See Nbond, Nbend, Nlbend, Nofpb, Ntors.
Optional. See Sec. 1.15.
- ◇ Keyword - SYMMETRY
- ◇ Description - use symmetry internal coordinates.
Required if you are using redundant internal coordinates. See Sec. 1.16. Isymm.
- ◇ Keyword - RESTRICTED
- ◇ Subsidiary - ENERGY, DIPOLE
- ◇ Description - the specified input expansion is taken to be a restricted (Nielsen-type) expansion. Can also be used for “unweighting” the inputs. See Sec. 1.18, Iparmf, Iparmd.
- ◇ Keyword - HARMONIC
- ◇ Description - reads in a new set of harmonic frequencies.
Optional. See Sec. 1.13, Nwfrq.

- ◇ Keyword - FIT
- ◇ Description - performs a least squares fit (varying the harmonic frequencies).
Optional. See Sec. 1.24, Ilsqrs.
- ◇ Keyword - ALIGN
- ◇ Description - allows the user to align degenerate modes.
May be necessary for spherical tops. See Sec. 1.23 and Idegnl.
- ◇ Keyword - CORIOLIS, FERMI, DARLING-DENNISON
- ◇ Subsidiary - [NUMBER], TOLERANCE, TOLERANCES
- ◇ Description - tells the program whether to account for resonances, and whether to adjust the resonance-test tolerances. Optional, but indicated if resonances are strong. The [NUMBER] is used to distinguish between the two types of Fermi resonances. See Sec. 1.14, Icoril, Iferm1, Iferm2, Idarl.
- ◇ Keyword - LABELLING
- ◇ Description - allows the frequencies to be re-labelled.
Optional. See Sec. 1.11 and Ifreq.
- ◇ Keyword - PROJECT
- ◇ Subsidiary - [NUMBER]
- ◇ Description - project out translation and rotation from the specified degree of the potential. (Same as Irotrn = [NUMBER]).
Optional.
- ◇ Keyword - CURVILINEAR
- ◇ Description - allows for the use of curvilinear normal coordinates. (Same as Icurvq=1).
Optional. See Appendix E and Reference 11. Before using this option, consult the authors.
- ◇ Keyword - AVERAGED
- ◇ Description - calculates vibrationally-averaged properties. (Same as Iaverg=1).
Optional. See App. J.
- ◇ Keyword - REPRESENTATION
- ◇ Subsidiary - [NUMBER]

- ◇ Description - Defines how the principal axes are related to the original axes e.g. Ir, I_{rr}, etc. Used in calculating the centrifugal distortion constants. Optional. See App. H. (Same as Irep = [NUMBER]).
- ◇ Keyword - PRINTFILE, PRINT, PRINTALL
- ◇ Subsidiary - [NUMBER]
- ◇ Description - PRINTFILE creates a new print file template, Sec. 1.12. PRINT changes the amount of data printed ([NUMBER]=0 gives the least output, 2 the most; equivalent to Iprint.) PRINTALL prints all output. Optional.
- ◇ Keyword - PLIVA
- ◇ Description - uses the new anharmonic constant formulae of Pliva [13] for symmetric tops. This can only be run from the keyword input. See App. K. Optional. Recommended for molecules with high order symmetry axes.
- ◇ Keyword - TEMPERATURE, MOMENTUM
- ◇ Subsidiary - [NUMBER]
- ◇ Description - the temperature and the maximum total angular momentum to use. (Same as Itemp and Maxj). MOMENTUM controls the number of rotational term values calculated. Optional.
- ◇ Keyword - END
- ◇ Description - ends the input deck.
- ◇ Output Title.
An appropriate title can be given to any run of SPECTRO under the banner TITLE.
- ⊙ Example:


```
# TITLE ##
H2O2DZP ANALYSIS
```

1.7 Geometry Input.

- ◇ Input of atomic positions and atomic numbers.
- ◇ Keyword = GEOMETRY (Igeom).
- ◇ Subsidiary keyword = CARTESIAN.

⊙ Format

```
# GEOM ##
Natom      Ibohr
Chg(1)     X(1)      Y(1)      Z(1)
Chg(2)     X(2)      Y(2)      Z(2)
.....
Chg(Natom) X(Natom) Y(Natom) Z(Natom)
```

Natom is the total number of atoms in the molecule;

Ibohr specifies whether the geometry is in units of Å(0) or a₀(1);

Chg(n) is the atomic number of the atom labelled n;

X(n), Y(n) and Z(n) are the cartesian coordinates of the atom labelled n.

⊙ Example: hydrogen peroxide geometry in a₀ with the two oxygen atoms specified first.

```
# GEOM ##
  4      1
8.0    -1.31323614    0.0    0.0
8.0     1.31323614    0.0    0.0
1.0    -1.70920569   -1.46340287    0.94913178
1.0     1.70920569    1.46340287    0.94913178
```

◇ Subsidiary keyword = TAPE.

◇ Reads geometry from fortran unit 10.

Same format as above with out the banner.

◇ Important note.

For correct results the Cartesian axis system of the force field must be **identical** to that of the geometry.

◇ Subsidiary keyword = INTERNAL.

◇ Reads an internal coordinate geometry.

This cannot be used with a cartesian potential expansion.

⊙ Format

```
# ZMAT ##
Inum(1)  Ianz(1) /
Inum(2)  Iz(2,1) Bl(2) Ianz(2) /
Inum(3)  Iz(3,1) Bl(3) Iz(3,2) Alp(3) Ianz(3) /
Inum(4)  Iz(4,1) Bl(4) Iz(4,2) Alp(4) Iz(4,3) Bet(4) Iz(4,4) Ianz(4) /
0 /
```

Inum(n) is an integer labelling the atom n;

Ianz(n) is the atomic number of atom n;

Iz(n,1) is an integer labelling the first atom to which atom n is directly bonded;

Bl(n) is the length of the bond Inum(n)-Iz(n,1);

Iz(n,2) labels the next atom to which atom n is attached, this time not directly but through another atom;

Alp(n) is the angle between the bonds Inum(n)-Iz(n,1)-Iz(n,2);

Iz(n,3) labels the atom which forms a dihedral angle with atom n;

Bet(n) is the value of the above dihedral angle;

Iz(n,4) normally has the values 0 or 1. If it is zero then Iz(n,3) and Bet(n) have the definitions given above. Sometimes, however, it is simpler to use a second bond angle to create a dihedral angle. Hence, if Iz(n,4) has the value one, then Iz(n,3) specifies the nucleus for which the second internuclear angle, whose value is given by Bet(n), is given. The final card, after completion of geometry input, is Inum(n) = 0.

◇ It is also possible to use dummy atoms by specifying Ianz(n) = 0.

⊙ Example: hydrogen peroxide geometry with the two oxygen atoms specified first.

```
# ZMAT ##
1 8 /
2 1 1.452 8 /
3 1 0.965 2 100.0 1 /
4 2 0.965 1 100.0 3 119.1 0 1 /
0 /
```

1.8 Symmetric Top Rotation.

◇ For symmetric tops we must align the molecular geometry to obey spectroscopic convention. A rotation is performed to put one of the atoms (not the central atom) on the x-axis. This atom is specified in File 5:

⊙ Format.

```
# IROTN ##
Iauto Iat1 Norder
```

Iauto is set equal to one to perform the automatic alignment. Iat1 specifies the atom to be rotated onto the x-axis. Norder is the order of the highest rotation axis in the molecule (it should be negative if the highest axis is an improper rotation). For example Norder=3 for ammonia, but Norder=-4 for allene. For more information about degenerate mode alignment, see section 1.23.

1.9 Cartesian Fields.

- ◇ This section describes the input of Cartesian force constants and dipole derivatives.
- ◇ Keyword = DERIVATIVE (Nderiv).
- ◇ Subsidiary keyword = ENERGY.
- ◇ NUMBER.

This section describes how the second, third and fourth derivative Cartesian force constants are input. They should have atomic units (Hartree, bohr). Three numbers are read on each line.

The Cartesian second derivatives (represented by the matrix FX) can be read in in two formats.

(1). The first is the HONDO [10] format used by CADPAC. To use this format, use the subsidiary keyword PUNCH (or set the value of Nderiv to be negative i.e., -2,-3,-4). File 15, which contains the second derivatives, should be of the form

⊙ Format.

FX(J,3I-2) FX(J,3I-1) FX(J,3I)

i.e. in the order

FX(1,1)	FX(1,2)	FX(1,3)
FX(2,1)	FX(2,2)	FX(2,3)
....		
FX(N3N,1)	FX(N3N,2)	FX(N3N,3)
FX(1,4)	FX(1,5)	FX(1,6)
FX(2,4)	FX(2,5)	FX(2,6)
....		

J takes the values 1 to N3N where N3N is equal to three times the number of atoms - the order of cartesian components is always 1(x), 1(y), 1(z) ... and not 1(x), 2(x) ...; J varies most rapidly.

I takes the values 1 to Natom where Natom is equal to the number of atoms.

FX(J, K) is the value of the particular force constant.

(2). The Cartesian second derivatives should be in the order:

⊙ Format.

```

FX(1,1)    FX(1,2)    FX(1,3)
FX(1,4)    FX(1,5)    FX(1,6)
.....
FX(1,N3N-2)  FX(1,N3N-1)  FX(1,N3N)
FX(2,1)     FX(2,2)     FX(2,3)
.....

```

◇ Third derivatives.

The input for the cartesian third derivatives in File 30 should be of the form

⊙ Format.

```

F33(1)    F33(2)    F33(3)
F33(4)    .....    F33(I3N3N)

```

where

$$I3N3N = \frac{N3N(N3N + 1)(N3N + 2)}{6}$$

that is the elements of the cartesian third derivative force field are stored in a one-dimensional array whose index is computed from the three mode labels. The index for the element f_{ijk} , sorted so $i \leq j \leq k$ is given by

$$i + \frac{(j-1)j}{2} + \frac{(k-1)k(k+1)}{6}$$

◇ Fourth derivatives.

That for the Cartesian fourth derivatives in File 40 is of the form

⊙ Format.

```

F44(1)    F44(2)    F44(3)
F44(4)    .....    F44(I4N3N)

```

where in a manner analogous to the third derivatives

$$I4N3N = \frac{N3N(N3N + 1)(N3N + 2)(N3N + 3)}{24}$$

and the index is

$$i + \frac{(j-1)j}{2} + \frac{(k-1)k(k+1)}{6} + \frac{(l-1)l(l+1)(l+2)}{24}$$

- ◇ Dipole fields.
- ◇ Subsidiary keyword = DIPOLE (Nprop).
- ◇ NUMBER.

Cartesian dipole moment derivatives are read in from the files below:

```
File65    first derivatives
File66    second derivatives
File67    third derivatives
```

All of the Cartesian dipole moment derivatives must be in atomic units. Note that the dipole field must be expressed in the same coordinate system as the force field; to use a Cartesian dipole field, you must also input a Cartesian force field.

- ◇ First derivatives.

```
A1(1)      A1(2)      A1(3)
Dip1c(I,1) Dip1c(I,2) Dip1c(I,3)
```

where A1(1), A1(2) and A1(3) are the three components of the equilibrium dipole moment; Dip1c(I,IX) are the three components of the first derivative with respect to the displacement I. I takes the values 1 to N3N; again the coordinates are in the order 1x,1y,1z,2x,... not 1x,2x,....

- ◇ Second derivatives.

```
IX
Dip2c(I,J,IX)
```

J takes the values 1 to N3N and varies the quickest, I also varies from 1 to N3N. The data is read in three blocks, for IX=1,2,3 (X,Y,Z).

Dip2c(I,J,IX) are the components of the cartesian second derivative.

- ◇ Third derivatives.

```
IX
Dip3c(I)
```

I takes the values 1 to I3N3N. There are again three blocks of derivatives for IX=1,2,3.

Dip3c(I) are the cartesian third derivative components. The index I is the index of three mode labels defined on the previous page.

- ◇ Polarisability fields.
- ◇ Subsidiary keyword = POLARISABILITY.

◇ Alternative keyword = POLARIZABILITY.

◇ NUMBER.

Cartesian polarisability derivatives are read in from the files below:

```
File71    first derivatives
File72    second derivatives
```

The first derivatives should be in the format:

◇ First derivatives.

```
A1(J,1,1)    A1(J,1,2)    A1(J,1,3)
A1(J,2,1)    A1(J,2,2)    A1(J,2,3)
A1(J,3,1)    A1(J,3,2)    A1(J,3,3)
```

where A1(J,1,1) is the first component of the derivative polarisability, i.e. α_{xx}^J . J takes the values 1 to N3N.

The second derivatives should be in the format:

◇ First derivatives.

```
A2(J,K,1,1)  A2(J,K,1,2)  A2(J,K,1,3)
A2(J,K,2,1)  A2(J,K,2,2)  A2(J,K,2,3)
A2(J,K,3,1)  A2(J,K,3,2)  A2(J,K,3,3)
```

where A2(J,K,1,1) is the first component of the second derivative polarisability, i.e. α_{xx}^{JK} . J and K take the values 1 to N3N.

◇ Hyperpolarisability fields.

◇ Subsidiary keyword = HYPERPOLARISABILITY.

◇ Alternative keyword = HYPERPOLARIZABILITY.

◇ NUMBER.

Cartesian hyperpolarisability derivatives are read in from the files below:

```
File75    first derivatives
```

The derivatives should be in the format:

◇ First derivatives.

B1(J,1,1,1)	B1(J,1,2,1)	B1(J,1,3,1)
B1(J,2,1,1)	B1(J,2,2,1)	B1(J,2,3,1)
B1(J,3,1,1)	B1(J,3,2,1)	B1(J,3,3,1)
B1(J,1,1,2)	B1(J,1,2,2)	B1(J,1,3,2)
B1(J,2,1,2)	B1(J,2,2,2)	B1(J,2,3,2)
B1(J,3,1,2)	B1(J,3,2,2)	B1(J,3,3,2)
B1(J,1,1,3)	B1(J,1,2,3)	B1(J,1,3,3)
B1(J,2,1,3)	B1(J,2,2,3)	B1(J,2,3,3)
B1(J,3,1,3)	B1(J,3,2,3)	B1(J,3,3,3)

where B1(J,1,1,1) is the first component of the derivative hyperpolarisability, i.e. β_{xxx}^J .
J takes the values 1 to N3N.

1.10 Isotopic Substitution.

- ◇ This section describes the use of isotopes (other than the most common isotopes of each element, which are the defaults).
- ◇ Keyword = ISOTOPE(Isotop).

The atomic masses listed under WEIGHT in file 5 are substituted for the default masses of the specified atoms.

⊙ Format.

```
# WEIGHT ##
Nchg
J    W(J)
```

Nchg specifies the number of isotopic changes to be made;

J labels the atom for which a different isotope is to be used;

W(J) is the value of the atomic mass of this isotope in a.m.u..

The default values of the atomic masses used by the program are given in subroutine DIST.

⊙ Example: to calculate constants for HOOD instead of HOOH.

```
# WEIGHT ##
1
4    2.014101779
```

1.11 Change Of Labelling.

- ◇ Keyword = LABELLING (Ifreq).

◇ NUMBER.

This allows one to label the frequencies according to any particular convention. By default, the labels increase with decreasing frequency.

⊙ Format.

```
# LABELS ##  
Iold   Inew
```

Iold is the old label;

Inew is the new label.

⊙ Example: to relabel five modes, use the keyword sentence LABELLING FIVE FREQS or in the Integer Input set Ifreq=5. Then in File 5 put:

```
# LABELS ##  
  3    2  
  5    3  
  6    4  
  2    5  
  4    6
```

1.12 Print Control File.

◇ Keyword = PRINTFILE.

The output can be controlled by use of a print file, FORTRAN unit 8. First create the template for this file by putting the word PRINTFILE in the keyword input. The program will then stop after printing the template in File 8. The user should then edit File 8, inserting a character, e.g. (*), to the right of the output data required. After editing File 8, delete the keyword PRINTFILE in File 7, and run SPECTRO again. This time the program will run normally, but only the desired output will be printed.

1.13 New Harmonic Frequencies.

◇ Keyword = HARMONIC.

This option allows for the input of a particular set of harmonic frequencies in a calculation, e.g. experimental frequencies, to replace those calculated from the quadratic force field. The input frequencies are in units of cm^{-1} . In File 5 input:

⊙ Format.

```
# NWFRQ ##  
Freq(I)
```

I takes the values 1 to Nvib. A full set of new harmonic frequencies is read in.

1.14 Resonance.

- ◇ Keywords = CORIOLIS (Icoril), FERMI(Iferm1, Iferm2), DARLING-DENNISON (Idarl).
- ◇ NUMBER.
- ◇ Subsidiary keyword = TOLERANCES.

When SPECTRO is first run it will notify the user of any apparent resonances satisfying the tolerances detailed below. If one wishes to take any of these into account, then the code must be run again with the input specified in this section. Taking a resonance "into account" means removing the relevant terms with near-zero denominators from the perturbation theory. In simple cases the program also forms and diagonalizes some of the matrices which result from treating the resonance interaction as an off-diagonal matrix element instead of in the perturbation sums.

⊙ Format.

```
# FERMI1 ##
Nferm1
Ivib(i)   Jvib(i)
Ftol1
F3tol
```

Nferm1 is the number of Fermi resonances of the type $2\omega_i \sim \omega_j$; $i=1$ to Nferm1;

Ivib, Jvib are the modes involved in the resonance. All of the tolerances (e.g. Ftol1, F3tol) need only be input if the keyword TOLERANCES (or, for example, Iferm1=2) is used, and are discussed below.

⊙ Example: stretch-bend resonance between mode 1 and mode 2 in water

```
# FERMI1 ##
1
2   1
```

if you have input the keyword sentence FERMI TYPE 1.

⊙ Format.

```
# FERMI2 ##
Nferm2
Jvib(i)   Kvib(i)   Ivib(i)
Dftol
Dltol
```

Nferm2 is the number of Fermi resonances of the type $\omega_i \sim \omega_j + \omega_k$ $j \neq k$;

where Ivib, Jvib, Kvib are the modes involved in the resonance and $i=1, Nferm2$.

⊙ Format.

```

# CORIOL ##
Ncoril
Ncorst(i)
Ivib   Jvib   Iaxis   Ibxis   Icxis
Ivk(i,i1) (i1=1,number of non-degenerate modes)
Ivl(i,i2) (i2=1,N2dm)
Ill(i,i2) (i2=1,N2dm)
Ctol
Ztol

```

Ncoril is the number of Coriolis resonances.

Ncorst(i) controls the vibrational states between which the matrix element of H_{21} is computed for each resonance. If Ncorst(i)=0, the matrix element between the fundamentals is calculated by default, and you needn't input Ivk, Ivl, and Ill. By setting Ncorst(i)=1, you can specify vibrational states other than the fundamentals by specifying one of the vibrational states with Ivk, Ivl, and Ill. Ncorst must be set to zero for spherical tops.

i runs from 1 to Ncoril.

Ivib, Jvib are the modes in resonance.

Iaxis, Ibxis, Icxis take the value one if the resonance is about that axis.

Ivk(i,i1) is the number of quanta in each non-degenerate mode;

Ivl(i,i2) is the number of quanta in each doubly-degenerate mode;

Ill(i,i2) is the number of vibrational angular momentum quanta in each doubly degenerate mode;

Ivl and Ill should not be input for asymmetric top molecules. At present only certain types of Coriolis matrix elements are calculated for symmetric tops.

The other vibrational state involved has the same vibrational quantum numbers, but one more quantum in mode Ivib and one fewer quantum in mode Jvib.

For example, if you would like to take into account the effects of both you could input the keyword CORIOLIS and in File 5:

- ⊙ Example: an A-type Coriolis resonance between modes 4 and 6 and a C-type Coriolis resonance between modes 1 and 5

```

# CORIOL ##
2
0
4 6 1 0 0
0
1 5 0 0 1

```

For Darling-Dennison resonances:

- ⊙ Format.

```
# DARLING ##
Ndarl
Ivib(i)   Jvib(i)
Ddtol
```

Ndarl is the number of Darling-Dennison resonances; $i=1,Ndarl$;
Ivib, Jvib are the modes in resonance.

⊙ Example: a Darling-Dennison resonance in formaldehyde between modes 1 and 5

```
# DARLING ##
      1
      1   5
```

Further testing for Fermi, Coriolis or Darling-Dennison resonances may be done within certain restrictions by using the subsidiary keyword TOLERANCES (or by setting Iferm1, Iferm2, Icoril or Idarl equal to 2). Otherwise no tolerances need be input. The input must then include tolerances for the selected type of resonance given by:

◇ For Coriolis resonance Ctol and Ztol.

These give the largest frequency difference and smallest Coriolis constant to be considered, respectively;

◇ For Fermi type 1 resonance Ftoll and F3tol.

Ftoll is the largest frequency difference between the frequencies $2\omega_i$ and ω_j . F3tol is the smallest cubic force constant to be considered connecting the frequencies in resonance;

◇ For Fermi type 2 resonance Dftol and Dltol.

Dftol is the largest value of the energy denominator Ω_{ijk} and Dltol the largest individual frequency difference of the type $\omega_i \sim \omega_j + \omega_k$. Note that an amended value of F3tol, the smallest cubic force constant considered, may be set using the Fermi type 1 input if required.

◇ For Darling-Dennison resonance Ddtol.

For Darling-Dennison resonance Ddtol is the largest frequency difference between the frequencies $2\omega_i$ and $2\omega_j$.

◇ Default values for all of these tolerances can be found in the subroutine RESTST. All current values of the tolerances are printed out in the output.

1.15 Internal Coordinates.

◇ Keywords = STRETCH,BEND,LINEAR,PLANE,TORSION.

◇ Alternate Keywords = STRETCHES,BENDS,TORSIONS.

◇ NUMBER.

This section describes how a set of internal coordinates is specified for a molecule. The number of internal coordinates to be defined is given by the value of $N_{\text{bond}} + N_{\text{bend}} + 2 \cdot N_{\text{lbend}} + N_{\text{ofpb}} + N_{\text{tors}}$. This value may be larger than $3N-6$ (or $3N-5$ for a linear molecule) if required by the definitions of symmetry internal coordinates, Sec. 1.16. That is, redundant coordinates may be used. Note that you only specify one component of each linear bend (the program knows that they come in pairs).

⊙ Format.

```
# CURVIL ##
Ibond(1,I)  Ibond(2,I)
Ibend(1,I)  Ibend(2,I)  Ibend(3,I)
Ilbend(1,I) Ilbend(2,I)  Ilbend(3,I)
Iofpb(1,I)  Iofpb(2,I)  Iofpb(3,I)  Iofpb(4,I)
Itors(1,I)  Itors(2,I)  Itors(3,I)  Itors(4,I)
```

Ibond labels two atoms between which there is a bond;

Ibend labels three atoms defining a non-linear angle;

Ilbend labels three atoms defining a linear angle;

Iofpb labels four atoms defining a plane; → *the first atom is the central atom*

Itors labels four atoms defining a torsional angle.

The number of each internal coordinate to be read in is specified in the main input. For an angle, the first atom input is the central atom (following Hoy, Mills, and Strey's convention [2]). All bond stretches must be specified first, then non-linear bends, then linear bends, then out-of-plane bends and finally torsions.

⊙ Example: hydrogen peroxide, which has 3 stretches, two bends and a torsion

```
# CURVIL ##
 1  2
 1  3
 2  4
 1  2  3
 2  1  4
 3  1  2  4
```

1.16 Symmetry Coordinates.

◇ Keyword = SYMMETRY (Isymm).

This section describes how symmetry internal coordinates can be defined in terms of internal coordinates. This input is required if redundant coordinates are used, and is

often convenient for comparisons with the spectroscopic literature. If this option is turned on (with the keyword or integer inputs) one must put the input detailed below in File 5.

⊙ Format.

```
# SYMCRD ##
  Isymm  Ncrs  Iscrs  K
```

Isymm is the index for the symmetry coordinate that we wish to construct;

Ncrs is the number of internal coordinates used in this symmetry coordinate;

Iscrs specifies the number of coordinates used to make the symmetry coordinate from a linear combination of ^{internal} symmetry coordinates; x

K determines how the normalisation constants of the symmetry coordinates are to be input when Iscrs \neq 0;

* Case

Iscrs = 0

The input file should be of the form

```
# SYMCRD ##
  Isymm  Ncrs  0  0
  Inorm  Icrd(J)
  0.0     Ifact(J)
```

J takes the values 1 to Ncrs;

Inorm determines the normalization constant, Fact, which is related to Inorm by the expression

$$Fact = \frac{1.0}{\sqrt{Inorm}}$$

Icrd(J) are the internal coordinates that make up the symmetry coordinate;

Ifact(J) is the way these internal coordinates combine to form the symmetry coordinate, i.e. the value of the factor multiplying each internal coordinate.

⊙ Example: hydrogen peroxide forming symmetric and antisymmetric stretch and bend coordinates (see CURVIL on the previous page) would be

```
# SYMCRD ##
  1  2  0  0
  2  2  3
  0.0 1  1
  2  2  0  0
  2  4  5
  0.0 1  1
  3  1  0  0
  1  1
  0.0 1
```

```

4  2  0  0
2  2  3
0.0 1 -1
5  2  0  0
2  4  5
0.0 1 -1
6  1  0  0
1  6
0.0 1

```

The cases discussed in the rest of this section are for particularly complicated forms of symmetry coordinates used in specialized references.

```

* Case 2
  Iscrs ≠ 0
  # SYMCRD ##
  Isymm  Ncrs  Iscrs  K
  Nc(L)

```

L takes the values 1 to Iscrs;

Nc(L) is the number of internal coordinates in each symmetry coordinate of the linear combination;

If $K < 0$ then the normalisation constants of the symmetry coordinates of the linear combination are input as real numbers;

If $K = 0$ then they are input as integers;

If $K > 0$ then they are formed using P, Q and K (C_{3v} molecules only).

```

* Case 2a
  K < 0
  The input file must be of the form:
  # SYMCRD ##
  Isymm  Ncrs  Iscrs  K
  Nc(L)
  Rnm(L)  Icd(L,J)
  Temp    Ift(L,J)
  Inm     Lincmb(L)

```

L takes the values 1 to Iscrs and J takes the values 1 to Ncrs.

Rnm(L) is the normalisation constant for each symmetry coordinate of the linear combination;

Icd(L,J) are the internal coordinates that make up each symmetry coordinate of the linear combination;

Ift(L,J) are the factors multiplying each symmetry coordinate of each linear combination;

Inm determines the normalisation constant of the linear combination of symmetry coordinates under construction, given by

$$Anorm = \frac{1.0D0}{\sqrt{Inm}}$$

Lincmb(L) denotes the particular linear combination of symmetry coordinates.

* Case 2b

$$K = 0$$

The input file is of the form

```
# SYMCRD ##
Isymm  Ncrs  Iscrs  0
Nc(L)
Inm(L)  Icd(L,J)
Temp    Ift(L,J)
Inm     Lincmb(L)
```

Inm(L) determines the normalisation constant for each symmetry coordinate of the linear combination

$$Rnm(L) = \frac{1.0D0}{\sqrt{Inm}}$$

where Inm(L) is, of course, an integer.

* Case 2c

$$K > 0$$

We use the P, Q and K to define the normalisation constants and then use values appropriate for C_{3V} molecules only. The input file is of the form

```
# SYMCRD ##
Isymm  Ncrs  Iscrs  K
Nc(L)
Inm     Icd(L,J)
Temp    Ift(L,J)
Icd1    Icd2
If1     If2     If3     If4
If5     If6     If7     If8
Inm     Lincmb(L)
```

Icd1 and Icd2 determine the value of K where

$$K = \frac{-3\sin\beta\cos\beta}{\sin\alpha}$$

where α and β are dependent upon Icd2 and Icd1 respectively;

If1 through to If8 determine the values of P and Q, given by

$$P = \frac{If1 + If2 * K}{\sqrt{If3 + If4 * K^2}}$$

$$Q = \frac{If5 + If6 * K}{\sqrt{If7 + If8 * K^2}}$$

Lincmb(L) are the factors of the symmetry coordinates of the linear combination.

1.17 Internal Coordinate Fields.

This section describes the input of force constants and dipole derivatives in internal coordinates. These inputs are read if the main keyword phrase (section 1.6) is 'INTERNAL NORMAL' or 'INTERNAL CARTESIAN'. The internal coordinates in SPECTRO are always in Å units for bond stretches and dimensionless units (e.g. radians) for the other types of internal coordinates.

- ◇ Keyword = DERIVATIVE (Nderiv).
- ◇ Subsidiary keyword = INTERNAL.
- ◇ Subsidiary keyword = ENERGY (Ncart).
- ◇ NUMBER.

This section describes the input of quadratic, cubic and quartic force constants in internal coordinates.

For second derivatives:

```
# F2INT ##
Nread
I   J   F2
```

For third derivatives:

```
# F3INT ##
Nread
I   J   K   F3
```

And for fourths:

```
# F4INT ##
Nread
I   J   K   L   F4
```

where Nread is the number of force constants of each order to be read in;

I, J, K and L are the internal coordinate labels ranging in value from 1 to the total number of internal coordinates;

F2, F3 and F4 are the values of the second, third and fourth derivative force constants F^{ij} , F^{ijk} , and F^{ijkl} . If symmetry coordinates are being used they are instead F_{ij} , F_{ijk} , and F_{ijkl} . The energy units are mdyne*Å=attojoules. Note that you should input only one of the permutation-related derivatives, e.g. under F2INT enter only:

```

3 4 0.543
not
3 4 0.543
4 3 0.543

```

Though SPECTRO knows that permutations of indices don't change derivatives, it does not know any other symmetries. Therefore you must input all three NH bond stretching quadratic force constants F'' in ammonia for example, even though they are equal.

◇ Subsidiary keyword = DIPOLE (Nprop).

◇ NUMBER.

A full cubic dipole can be input in internal coordinates as follows:

```

# DIPEQ ##
DIPEQ(1)  DIPEQ(2)  DIPEQ(3)

# DP1INT ##
Nread
I  DP1INT(I,1)  DP1INT(I,2)  DP1INT(I,3)

# DP2INT ##
Nread
I  J  DP2INT(IJ,1)  DP2INT(IJ,2)  DP2INT(IJ,3)

# DP3INT ##
Nread
I  J  K  DP3INT(IJK,1)  DP3INT(IJK,2)  DP3INT(IJK,3)

```

where Nread is the number of constants to be read in;

I, J and K are the internal coordinate labels;

1, 2 and 3 are the directions;

DIPEQ, DP1INT, DP2INT and DP3INT are the equilibrium and dipole derivative values. Dipole moments are in atomic units, internal coordinates are in Å (for bond lengths) or are dimensionless (for angles). If you are using symmetry coordinates, the derivatives read here are with respect to the symmetrized internals.

1.18 Restricted-Summation Taylor Expansions.

By default all of the expansions are unrestricted, as recommended in Ref. 2. However, much of the literature uses restricted summations, e.g. $i \leq j \leq k$. This option allows one to use these sorts of constants, i.e. when this option is switched on, the program begins by converting the input into the unrestricted constants used inside the program. Also,

sometimes "bond-length weighted" bend coordinates are used instead of the internal coordinates used in the program. This option allows one to undo any weightings or parameterizations in the input force or dipole fields. It can also be used to cope with strange unit systems. The RESTRICTED option can only be used when starting from an internal coordinate field.

◇ Keyword = RESTRICTED (Iparmf,Iparmd).

◇ Subsidiary keyword = ENERGY.

This section allows for restricted summations or scaling factors in the potential expansion.

⊙ Format.

```
# PARMF ##  
Nielsn   Ncordp   Itotp  
Icordp(I) Param(I)  
Totp
```

Nielsn is a positive, non-zero integer if the summations are restricted;

Ncordp is non-zero if some of the coordinates are weighted and some are not. Then it gives the number of coordinates to be unweighted;

Icordp(I) is the coordinate to be unweighted;

Param(I) is its weighting factor. Both Icordp(I) and Param(I) should only be given if Ncordp > 0. I runs from 1 to Ncordp.

Itotp is non-zero only if all weighting factors are themselves to be divided by a common factor; Totp is the value of this factor. Totp is only required if Itotp > 0.

◇ Subsidiary keyword = DIPOLE.

The format is identical to that for an energy field, except the banner is PARMD.

1.19 Vibrational states.

Calculates the vibrational energies of specified states. By default the code evaluates the energies of fundamentals, two-quantum combination bands and first overtones.

⊙ Format.

```
# VIBSTS ##  
Nstate  
I1sts(I,Nst)   I=1,N1dm (number of non-degenerate modes)  
I2sts(I,Nst)   I=1,N2dm  
I1sts(I,Nst)   I=1,N2dm
```

Nstate is the number of vibrational states to be read in; Nst=1,Nstate;

Ilsts contains the quantum numbers of the non-degenerate modes. I2sts contains those of the doubly degenerate modes and I1sts the values of the vibrational angular momentum quantum numbers. I2sts and I1sts are required only for symmetric tops.

- ⊙ Example: to evaluate the second, third and fourth overtones of the fourth mode of a six-mode asymmetric top

```
# VIBSTS ##
3
0 0 0 3 0 0
0 0 0 4 0 0
0 0 0 5 0 0
```

1.20 Vibrational band intensities.

SPECTRO allows calculation of the intensities of vibrational bands, given input dipole moment fields, by the second-order perturbation theory formulae presented in Reference 12. This option is switched on automatically by using the keyword DIPOLE (or by setting the Integer Input variable Nprop non-zero) and inputting at least a quadratic Cartesian dipole field. following

- ⊙ Format.

```
# INTEN ##
Iread  Icorrd
Vx
Toler1  Toler2
```

Iread instructs the program to read a new normal coordinate dipole field if set non-zero. Normally it is set to zero.

Icorrd is set equal to one if one wishes to account for the Coriolis term in the intensity calculations, zero otherwise.

Vx is the initial number of quanta in the mode which is changing in the transition. Normally this is set to zero. However, this can be used to calculate some hot-band transition dipoles by setting non-zero.

The two tolerances, Toler1 and Toler2, determine the cutoff point for resonance denominators in the intensity formulae. Toler1 applies to type 1 resonance and Toler2 applies to type 2 resonance. The test performed is:

Resonance denominator < Toler * Cubic force constant

Typically, Toler1 and Toler2 should be about equal to unity.

The first, second, and third derivatives of the dipole moment with respect to the Cartesian displacements must be input in file numbers 65, 66 and 67, using the format specified in Sect. 1.9.

The $\Delta v = 1$ and 2 transition dipoles are calculated. For the convenience of the user, some of these are converted to the corresponding integrated band intensities, though this conversion involves some approximations, as discussed in Reference 12. The program also does all the coordinate conversions on the dipole moment field that it does on the force field; in particular, one can use the program with the keyword sentence RUN INTERNAL TO CARTESIAN (Integer Input variable Ncart=5) to convert an internal-coordinate dipole moment field to a Cartesian field, and then run the program again, with the keyword sentence RUN CARTESIAN TO NORMAL (or Ncart =0, 1 or 99) to get the intensities. This would be necessary because it is not possible to run the intensity routine from an internal dipole field.

1.21 Electric Field Input.

- ◇ Input of cartesian components of the electric field.

This is required whenever the keyword FINITE is used. All three components of the field are input.

- Format.

```
# FIELD ##
FLD(1) FLD(2) FLD(3)
```

1.22 Degenerate Mode Labelling.

- ◇ Defines a labelling scheme for the vibrational modes.

This input is required whenever a molecule with degenerate modes is run; i.e. for all symmetric and spherical tops.

- Format.

```
# DEGMODE ##
N1dm    N2dm    N3dm
I1mode(I)    I=1,N1dm
I2mode(I,1)  I=1,N2dm
I2mode(I,2)  I=1,N2dm
I3mode(I,1)  I=1,N3dm
I3mode(I,2)  I=1,N3dm
I3mode(I,3)  I=1,N3dm
```

N1dm is the total number of singly degenerate modes;

N2dm is the total number of doubly degenerate modes;

N3dm is the total number of triply degenerate modes;

I1mode(I) labels the Ith singly degenerate mode;

I2mode(I,1) labels one component of the Ith doubly degenerate mode;

I3mode(I,1) labels one component of the Ith triply degenerate mode.

Referring to appendix K, I2mode(I,1) is the 'a' component and I2mode(I,2) is the 'b' component. I3mode(I,1) is the 'x' component, I3mode(I,2) the 'y' component and I3mode(I,3) the 'z' component.

The total number of modes ($3N-6$ or $3N-5$) is $N1_{dm}+2*N2_{dm}+3*N3_{dm}$.

1.23 Degenerate Normal Coordinate Alignment.

◇ Keyword = ALIGN (Idegnl).

◇ Symmetric and spherical tops only.

Takes linear combinations of the degenerate mode components to form new modes which are oriented according to convention (see appendix K). Under normal circumstances it will not be necessary to use this option for symmetric tops as automatic mode alignment can be performed. For automatic alignment, do not use the keyword ALIGN (if using Integer Input, set Idegnl=0). The automatic alignment routine considers modes which differ by less than 0.05cm^{-1} degenerate. Automatic alignment is done using the IROTN banner in File 5; for details see section 1.8.

In some cases however it will be necessary to use manual alignment, for example for spherical tops, or for symmetric tops with peculiar symmetries such that no reflection plane runs through an atom off the highest-order symmetry axis. Manual alignment is very tricky - it is recommended that users contact the authors in case of difficulty.

The direct effect of manual alignment is to change the LX and LXM matrices; this indirectly affects virtually all of the spectroscopic parameters. The desired form of the LXM matrix elements for the specified modes, atom, and x, y or z component ($ix=1,2,3$) are given in Icord(ix,imode,I), where I is the index running over the Ndegn different degeneracies in the molecule.

⊙ Format.

```
# DEGNL ##  
Ndegn  
Nmode(I)   Iatom(I)
```

then, for a doubly-degenerate mode (Nmode(I)=2):

```
ix  
Imode(1,I)   Imode(2,I)  
Icord(ix,1,I) Icord(ix,2,I)
```

while for a triply degenerate mode (Nmode(I)=3):

<code>Imode(1,I)</code>	<code>Imode(2,I)</code>	<code>Imode(3,I)</code>
<code>Icord(1,1,I)</code>	<code>Icord(1,2,I)</code>	<code>Icord(1,3,I)</code>
<code>Icord(2,1,I)</code>	<code>Icord(2,2,I)</code>	<code>Icord(2,3,I)</code>

This input is repeated for I values from 1 to Ndegn.

Nmode(I) is the degree of the Ith degeneracy;

Iatom(I) is the index of the atom whose motions will be considered in fixing the alignment;

Imode contains the labels of the modes involved in the degeneracy.

Only the x and y components of one atom's motion need be specified to fix a triply degenerate mode, and only the single ixth component need be specified to fix a doubly degenerate mode. Icord needn't be normalized, but at least one of the LXM matrix elements corresponding to the atom, ix component, and modes specified must be non-zero. Users have reported difficulty with spherical top alignment; consult the authors for the latest suggestions.

1.24 Least squares fitting.

- ◇ Keyword = FIT (Ilsqrs)
- ◇ This allows for the harmonic constants to be least squares fitted to experimental vibrational band origins, using *ab initio* anharmonic constants.

The File 5 input is given below for asymmetric tops and symmetric tops. Users wishing to least squares fit spherical tops should first consult the authors.

N.B. The authors believe that this is not the best way determine harmonic frequencies, since it does not use rotational and isotopic information.

⊙ Format.

```
# LSQRS ##
Nsts
Ist   Eng(I)   Iw
I1sts(J,I)   J=1,N1dm
I2sts(J,I)   J=1,N2dm
I1sts(J,I)   J=1,N2dm
```

Nsts is the number of experimental band origins to be used;

Ist labels a particular state;

Eng(I) is its (experimental) energy above zero point;

Iw should be set to zero;

I1sts is the number of quanta in each non-degenerate mode;

I2sts is the number of quanta in each doubly degenerate mode;

l_{vib} is the vibrational angular momentum in each doubly degenerate mode; Both l_{vib} and l_{rot} are only required if the number of doubly degenerate modes is greater than zero. l_{vib} varies from 1 to N_{vib} .

Appendix A

Analytic Derivatives in Quantum Chemistry.

Gradient theory is arguably the greatest advance of quantum chemistry in the period 1970-85. We draw attention to the following significant papers:

(a) P. Pulay, *Mol. Phys.* **17**, 197 (1969).

A presentation of analytic energy gradients (first derivatives) at the Self Consistent Field level.

(b) J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, *Int. Journal of Quant. Chem. Symp.* **13**, 225 (1979).

A presentation of analytic energy second derivatives at the Self Consistent Field level.

(c) J. F. Gaw, Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.* **81**, 6395 (1984).

A presentation of analytic energy third derivatives at the Self Consistent Field level.

(d) N. C. Handy and H. F. Schaefer, *J. Chem. Phys.* **81**, 5031 (1984).

Where it was shown that, for correlated wavefunction calculations, the full set of (3N) coupled equations do not need to be solved.

(e) N.C. Handy, R.D. Amos, J.F. Gaw, J.E. Rice, E.D. Simandiras, T.J. Lee, R.J. Harrison, G.B. Fitzgerald, and R.J. Bartlett, *NATO ASI Series*, **166**, 179 (1985);

N. C. Handy, R. D. Amos, J. F. Gaw, J. E. Rice and E. D. Simandiras, *Chem. Phys. Lett.* **120**, 151 (1985).

A presentation of analytic energy second derivatives at the MP2 level.

The development of these basic ideas to more general classes of wavefunctions has been aided by distinguished contributions from many leading scientists—several review articles have now been written. The situation is therefore that it is possible to determine, by analytic means, first, second and third derivatives of the energy, with respect to nuclear coordinates, by a variety of *ab initio* wavefunction methods. It will soon be possible to calculate fourth derivatives by analytic means, although today we calculate them by finite differences of third derivatives. By a similar method, up to third derivatives of the dipole moment with respect to nuclear coordinates may be calculated. Thus, in principle, the *ab initioist* may calculate the following forms for V and μ

$$V = \frac{1}{2} \sum f_{kl} \Delta x_k \Delta x_l + \frac{1}{6} \sum f_{klm} \Delta x_k \Delta x_l \Delta x_m + \frac{1}{24} \sum f_{klmn} \Delta x_k \Delta x_l \Delta x_m \Delta x_n \quad (\text{A.1})$$

$$\mu^\alpha = \mu_e^\alpha + \sum \mu_k^\alpha \Delta x_k + \frac{1}{2} \sum \mu_{kl}^\alpha \Delta x_k \Delta x_l + \frac{1}{6} \sum \mu_{klm}^\alpha \Delta x_k \Delta x_l \Delta x_m \quad (\text{A.2})$$

Appendix B

Perturbation Theory in Spectroscopy.

For many years, leading theoretical spectroscopists have also been attempting to derive values for the potential energy and dipole derivatives in equations (A.1) and (A.2). Their approach has been from the other end of the problem, that is from experimental infrared spectra. Their principal difficulty is the lack of sufficient data to determine all of the constants in equations (A.1) and (A.2). Accordingly, their approach essentially involves an approximate determination of the spectrum for assumed values of the constants in (A.1) and (A.2), and refinement by the method of least squares. The traditional approach has been to use second-order perturbation theory, built on the harmonic-oscillator/rigid-rotor approximation, and this is the approach used by SPECTRO. The starting point is one of Watson's forms [1] for the kinetic energy operator in normal coordinates. For example

$$\hat{T} = \frac{\hbar^2}{2} \sum \mu_{\alpha\beta} (\hat{J}_\alpha - \hat{\pi}_\alpha) (\hat{J}_\beta - \hat{\pi}_\beta) - \frac{1}{8} \hbar^2 \sum \mu_{\alpha\alpha} - \frac{\hbar^2}{2} \sum_k \frac{\partial^2}{\partial Q_k^2} \quad (\text{B.1})$$

and the above representations for V and μ .

This perturbation theory leads to expressions for observable spectroscopic constants in terms of the derivatives ab initioists can provide. In principle the derivation of these formulae is straightforward, but the algebra is complex and there are many subtle points. Many spectroscopists have contributed to the development of this theory over many years, and work continues to the present day. Much of this research is summarized in Ref. 6.

It is important to be aware of the situations where the perturbation theory approach breaks down. First, the Born-Oppenheimer approximation must be valid. so, for example, the approach may fail if two electronic surfaces intersect in the vicinity of the equilibrium geometry, as in the Renner-Teller molecule CO_2^+ . Second, the approach assumes that the molecule is fairly rigid and that the potential expansion is rapidly convergent; it will fail for floppy complexes, quasilinear molecules, and if there is a large amplitude motion such as an internal rotor. Third, the perturbation theory formulae fail if there is a resonance, i.e. if interacting states of the same symmetry have similar energies. Methods for dealing with resonances are discussed later.

Appendix C

The geometry, force field and dipole field.

To perform an anharmonic vibration-rotation analysis, the program could use following data:
(1) the masses m_i and cartesian coordinates of the equilibrium geometry, $r_{\alpha i}^e$ ($\alpha = x, y, z$), for each of the N nuclei;
(2) the cartesian displacement force field V given to quartic level by:

$$V = \frac{1}{2} \sum f_{kl} \Delta x_k \Delta x_l + \frac{1}{6} \sum f_{klm} \Delta x_k \Delta x_l \Delta x_m + \frac{1}{24} \sum f_{klmn} \Delta x_k \Delta x_l \Delta x_m \Delta x_n \quad (\text{C.1})$$

where the Δx_k ($k=1, 2, \dots, 3N$) denote the $3N$ cartesian displacement coordinates defined by

$$r_{\alpha k} - r_{\alpha k}^e \quad (\text{C.2})$$

with respect to local cartesian axes.

(3) for the prediction of infrared intensities, a dipole surface is required

$$\mu^\alpha = \mu_e^\alpha + \sum \mu_k^\alpha \Delta x_k + \frac{1}{2} \sum \mu_{kl}^\alpha \Delta x_k \Delta x_l + \frac{1}{6} \sum \mu_{klm}^\alpha \Delta x_k \Delta x_l \Delta x_m \quad (\text{C.3})$$

Note that all the summations in this manual are unrestricted unless stated otherwise.

Appendix D

Transition states

It is possible to use SPECTRO to calculate the spectroscopic constants of a molecule at a non-degenerate transition state. When the program finds a single negative force constant, greater in magnitude than $0.001 \frac{\text{mdyn}}{\text{A}}$, then it uses amended formulae to calculate the vibration-rotation interaction constants and anharmonic constants. These allow for the fact that one frequency is imaginary. An indication is provided in the output when a transition state calculation is being performed.

Appendix E

Curvilinear internal coordinates.

Instead of cartesian displacement coordinates, it is often more convenient to use curvilinear internal coordinates s_i ($i = 1, 2, \dots, 3N - 6$ ($3N - 5$ for linear molecules)). (The s_i are frequently denoted by a backwards R, the Cyrillic letter "yah".) They are represented in terms of Δx_k by

$$s_i = \sum B_i^k \Delta x_k + \frac{1}{2} \sum B_i^{kl} \Delta x_k \Delta x_l + \dots \quad (\text{E.1})$$

The s_i have been defined by Hoy, Mills and Strey [2] for:

(a) bond stretching (between atoms a and b)

$$s = |\mathbf{r}| - |\mathbf{r}^e| \quad (\text{E.2})$$

(b) angle bending (atom a bonded to atoms b and c through vectors \mathbf{r}_i and \mathbf{r}_j)

$$s = \arccos \left(\frac{\mathbf{r}_i \cdot \mathbf{r}_j}{r_i r_j} \right) - \arccos \left(\frac{\mathbf{r}_i^e \cdot \mathbf{r}_j^e}{r_i^e r_j^e} \right) \quad (\text{E.3})$$

(c) linear angle bending (atoms a, b and c all collinear)

$$s = \mathbf{e}_A \cdot \left(\frac{\mathbf{r}_i \wedge \mathbf{r}_j}{r_i r_j} \right) \quad (\text{E.4})$$

where \mathbf{e}_A is a vector perpendicular to the plane of vibration containing \mathbf{r}_i and \mathbf{r}_j

(d) out-of-plane bending (atoms b, c, d and a coplanar with a being the central atom connected to b, c and d by the vectors \mathbf{r}_i , \mathbf{r}_j and \mathbf{r}_k)

$$s = \left(\frac{\mathbf{r}_i \cdot \mathbf{r}_j \wedge \mathbf{r}_k}{r_i r_j r_k} \right) \quad (\text{E.5})$$

(e) torsion τ (atoms a and b linked by \mathbf{r}_i , b and c by \mathbf{r}_j and c and d by \mathbf{r}_k)

$$s = \pm \arcsin \left(\frac{\mathbf{r}_i \cdot \mathbf{r}_j \wedge \mathbf{r}_k}{r_i r_j r_k \sin \theta_{ij} \sin \theta_{jk}} \right) - \tau^{(e)} \quad (\text{E.6})$$

or the related formulae given by Hoy, Mills and Strey [2].

The potential energy may be expressed in terms of the curvilinear internal coordinates s

$$V = \frac{1}{2} \sum F^{ij} s_i s_j + \frac{1}{6} \sum F^{ijk} s_i s_j s_k + \frac{1}{24} \sum F^{ijkl} s_i s_j s_k s_l \quad (\text{E.7})$$

Appendix F

Normal coordinates.

Normal coordinates, denoted Q , are derived from the eigenvectors of the mass-weighted cartesian quadratic force constant matrix given by:

$$m^{-\frac{1}{2}} f m^{-\frac{1}{2}} \quad (\text{F.1})$$

and thus

$$\Delta x_k = \sum m_k^{-\frac{1}{2}} l_k^n Q_n \quad (k = 1, 2, \dots, 3N) \quad (\text{F.2})$$

$$Q_n = \sum l_n^k m_k^{\frac{1}{2}} \Delta x_k \quad (n = 1, 2, \dots, 3N - 6) \quad (\text{F.3})$$

In these coordinates the potential is

$$V = \frac{1}{2} \sum \lambda_r Q_r^2 + \frac{1}{6} \sum \Phi^{rst} Q_r Q_s Q_t + \frac{1}{24} \sum \Phi^{rstu} Q_r Q_s Q_t Q_u \quad (\text{F.4})$$

If we write V in wavenumber units, and introduce dimensionless normal coordinates q defined by

$$q_r = \left(\frac{2\pi c \omega_r}{\hbar} \right)^{\frac{1}{2}} Q_r \quad (\text{F.5})$$

then the form for V is

$$V = \frac{1}{2} \sum \omega_r q_r^2 + \frac{1}{6} \sum \phi^{rst} q_r q_s q_t + \frac{1}{24} \sum \phi^{rstu} q_r q_s q_t q_u \quad (\text{F.6})$$

where ω_r are the harmonic frequencies.

At this stage it is also convenient to write the relation between s and Q :

$$s_i = \sum L_i^r Q_r + \frac{1}{2} \sum L_i^{rs} Q_r Q_s + \frac{1}{6} \sum L_i^{rst} Q_r Q_s Q_t + \dots \quad (\text{F.7})$$

which defines the L tensor. Formulae for the L tensors for the cases of Appendix E are given in Hoy, Mills and Strey [2].

Appendix G

Symmetry coordinates.

For a molecule with symmetry, combinations of s_i may be derived which transform according to the irreducible representations of the group. Symmetry internal displacement coordinates are thus written

$$S_i = \sum U_i^j s_j \quad (\text{G.1})$$

where the U_i^j is defined separately for each molecule. In terms of S_i , V is expressed as

$$V = \frac{1}{2} \sum F_{ij} S_i S_j + \frac{1}{6} \sum F_{ijk} S_i S_j S_k + \frac{1}{24} \sum F_{ijkl} S_i S_j S_k S_l \quad (\text{G.2})$$

where F_{ij} is only non-zero if i and j belong to the same irreducible representation of the point group, etc.. The symmetry coordinates S are related to the normal coordinates Q through

$$S_i = \sum M_i^r Q_r + \frac{1}{2} \sum M_i^{rs} Q_r Q_s + \frac{1}{6} \sum M_i^{rst} Q_r Q_s Q_t + \dots \quad (\text{G.3})$$

where $M=UL$. Symmetry coordinates should be used when the ordinary internal coordinates would be redundant.

Symmetry coordinates are commonly used in the spectroscopic literature, particularly for symmetric top molecules. The conventions for C_{3v} symmetry coordinates are:

- the components of degenerate modes are symmetric and antisymmetric with respect to a plane through ABC, where A is the central atom, C lies along the C_3 axis (the Z axis) and B lies in the XZ plane.

In SPECTRO analogous conventions are used for all symmetric-top degenerate modes and the components are aligned this way automatically.

Appendix H

Anharmonic effects in the vibrations of asymmetric top molecules.

(a) Anharmonic constants and fundamental frequencies.

For an asymmetric top (a molecule with no degenerate vibrations), the vibrational energy levels are given by

$$E(\mathbf{v}) = \sum \omega_k (v_k + \frac{1}{2}) + \sum_{k \leq l} x_{kl} (v_k + \frac{1}{2})(v_l + \frac{1}{2}) + \dots \quad (\text{H.1})$$

So the fundamental frequency ν_i is given by

$$\nu_i = \omega_i + 2x_{ii} + \frac{1}{2} \sum_{k \neq i} x_{ik} \quad (\text{H.2})$$

The anharmonic constants are given by Ref. 3:

$$x_{kk} = \frac{1}{16} \phi^{kkkk} - \frac{1}{16} \sum_m (\phi^{kkm})^2 \left(\frac{8\omega_k^2 - 3\omega_m^2}{\omega_m(4\omega_k^2 - \omega_m^2)} \right) \quad (\text{H.3})$$

$$x_{kl} = \frac{1}{4} \phi^{kkl} - \sum_m \frac{\phi^{kkm} \phi^{llm}}{4\omega_m} - \sum_m \frac{(\phi^{klm})^2 \omega_m (\omega_k^2 + \omega_l^2 - \omega_m^2)}{2\Omega_{klm}} + \sum_\alpha B_\alpha (\zeta_{kl}^\alpha)^2 \left\{ \frac{\omega_k}{\omega_l} + \frac{\omega_l}{\omega_k} \right\} \quad (\text{H.4})$$

where we have used

$$\Omega_{klm} = (\omega_k + \omega_l + \omega_m)(-\omega_k + \omega_l + \omega_m)(\omega_k - \omega_l + \omega_m)(\omega_k + \omega_l - \omega_m) \quad (\text{H.5})$$

B_α are proportional to the reciprocal moments of inertia, given by

$$B_\alpha^e = \frac{h}{8\pi^2 c I_\alpha^e} \quad (\text{H.6})$$

and ζ_{jk}^α are the Coriolis constants derived from I by writing equation (F.2) as

$$\Delta r_{\alpha i} = m_i^{-\frac{1}{2}} \sum_n l_{i,\alpha}^n Q_n \quad (\text{H.7})$$

leading to

$$\zeta_{jk}^\alpha = \sum_i l_{i,\beta}^j l_{i,\gamma}^k - l_{i,\gamma}^j l_{i,\beta}^k \quad (\text{H.8})$$

It is appropriate at this time to discuss the transformation from a cartesian axis frame to a principal axis frame. This can be achieved in six different ways, namely:

1. Ir A -> Z B -> X C -> Y
2. IIr A -> Y B -> Z C -> X
3. IIIr A -> X B -> Y C -> Z
4. I1 A -> Z B -> Y C -> X
5. III1 A -> X B -> Z C -> Y
6. III1 A -> Y B -> X C -> Z

Each of these is a different representation and if a particular one is desired it can be selected by using a keyword phrase like REPRESENTATION FIVE or by setting the value of Irep in the main input to the representation required. The default representations are:

for asymmetric tops and prolate symmetric tops - Ir;

for oblate symmetric tops - IIIr.

(b) Anharmonic resonance.

Fermi resonance occurs whenever $2\omega_k \sim \omega_m$ or $\omega_k + \omega_l \sim \omega_m$ (or similar). SPECTRO will issue a warning if particular interaction appears to be resonant. If there is a Fermi resonance, following Califano [4], after writing the relevant terms in partial fractions, the divergent term is removed from x_{kk} and x_{kl} , which means that the relevant terms are replaced by

$$-\frac{\phi_{kkm}^2}{4} \left(\frac{1}{2\omega_m} + \frac{1}{8(2\omega_k + \omega_m)} \right) \quad (\text{H.9})$$

for x_{kk} and

$$-\frac{\phi_{klm}^2}{8} \left(\frac{1}{(\omega_k + \omega_l + \omega_m)} + \frac{1}{(\omega_k + \omega_m - \omega_l)} + \frac{1}{(\omega_l - \omega_k + \omega_m)} \right) \quad (\text{H.10})$$

for x_{kl} . A 2 by 2 matrix is then constructed for which the diagonal elements are given by the modified x_{kk} and x_{kl} , and the off-diagonal elements are given by

$$\langle v_k, v_l, v_m | H | v_k + 1, v_l + 1, v_m - 1 \rangle = \phi_{klm} \left(\frac{v_m(v_k + 1)(v_l + 1)}{8} \right)^{\frac{1}{2}} \quad (\text{H.11})$$

(e.g. $v_k, v_l, v_m = 0, 0, 1$) or

$$\langle v_k, v_m | H | v_k + 2, v_m - 1 \rangle = \frac{\phi_{kkm}}{2} \left(\frac{(v_k + 1)(v_k + 2)v_m}{2} \right)^{\frac{1}{2}} \quad (\text{H.12})$$

(e.g. $v_k, v_m = 0, 1$). In this way, the effects of Fermi resonance may be taken into account for both the fundamentals and overtones. If a single state is involved in more than one resonance, the user must diagonalize the larger matrix separately, but SPECTRO will provide the required matrix elements.

(c) Quartic and sextic centrifugal distortion constants.

The effective rotational Hamiltonian, H_{rot} , may be expanded for a rotating molecule as

$$H_{rot} = \sum B_\alpha \hat{J}_\alpha^2 + \sum_{p+q+r}^{even} h_{pqr} (\hat{J}_x^p \hat{J}_y^q \hat{J}_z^r + \hat{J}_z^r \hat{J}_y^q \hat{J}_x^p) \quad (H.13)$$

If $n (= p + q + r)$ is equal to four, then the h_{pqr} are the quartic centrifugal distortion constants and, if n is six, then they are the sextic distortion constants. Symmetry considerably reduces the number of independent h_{pqr} .

The basic form of the relevant quartic centrifugal Hamiltonian is

$$H_4 = \frac{1}{4} \sum \tau_{\alpha\beta\gamma\delta} \hat{J}_\alpha \hat{J}_\beta \hat{J}_\gamma \hat{J}_\delta \quad (H.14)$$

where

$$\tau_{\alpha\beta\gamma\delta} = \frac{-\hbar^4}{2hcI_\alpha I_\beta I_\gamma I_\delta} \sum \frac{a_k^{\alpha\beta} a_k^{\gamma\delta}}{\lambda_k} \quad (H.15)$$

in which

$$a_k^{\alpha\beta} = \left(\frac{\partial I_{\alpha\beta}}{\partial Q_k} \right)_e \quad (H.16)$$

An explicit expression for $a_k^{\alpha\beta}$ is written in terms of \mathbf{L} as follows

$$a_k^{\alpha\beta} = 2 \sum_i m_i^{\frac{1}{2}} \left(\delta_{\alpha\beta} \sum_\gamma r_{i\gamma}^e l_{i\gamma}^k - r_{i\alpha}^e l_{i\beta}^k \right) \quad (H.17)$$

Equation (H.14) is often written

$$H_4 = -D_J \hat{J}^4 - D_{JK} \hat{J}^2 \hat{J}_z^2 - D_K \hat{J}_z^4 + d_1 \hat{J}^2 (\hat{J}_+^2 + \hat{J}_-^2) + d_2 (\hat{J}_+^2 + \hat{J}_-^2) \quad (H.18)$$

It may be shown that a convenient way to express H_{rot} up to sextic terms is as follows

$$H_{rot} = \sum B_\alpha \hat{J}_\alpha^2 + \sum T_{\alpha\beta} \hat{J}_\alpha^2 \hat{J}_\beta^2 + \sum \Phi_{\alpha\alpha\alpha} \hat{J}_\alpha^6 \quad (H.19)$$

$$+ \sum_{\alpha \neq \beta} \Phi_{\alpha\alpha\beta} (\hat{J}_\alpha^4 \hat{J}_\beta^2 + \hat{J}_\beta^4 \hat{J}_\alpha^2) + \Phi_{xyz} (\hat{J}_x^2 \hat{J}_y^2 \hat{J}_z^2 + \hat{J}_z^2 \hat{J}_y^2 \hat{J}_x^2)$$

The sextic constants Φ , besides involving τ , also involve the third order force constants ϕ_{lmn} . General expressions for T and Φ may be found in Ref. 5, for example

$$T_{\alpha\alpha} = \frac{1}{4} \tau_{\alpha\alpha\alpha\alpha} \quad (H.20)$$

$$T_{\alpha\beta} = \frac{1}{4} (\tau_{\alpha\alpha\beta\beta} + \tau_{\beta\beta\alpha\alpha}) \quad (H.21)$$

The usual representation of the sextic Hamiltonian is

$$H_6 = H_J \hat{J}^6 + H_{JK} \hat{J}^4 \hat{J}_z^2 + H_{KJ} \hat{J}^2 \hat{J}_z^4 + H_K \hat{J}_z^6 + h_J \hat{J}^4 (\hat{J}_+^2 + \hat{J}_-^2)$$

$$+ \frac{1}{2} h_{JK} \hat{J}^2 \{ \hat{J}_z^2 (\hat{J}_+^2 + \hat{J}_-^2) + (\hat{J}_+^2 + \hat{J}_-^2) \hat{J}_z^2 \}$$

$$+ \frac{1}{2} h_K \{ \hat{J}_z^4 (\hat{J}_+^2 + \hat{J}_-^2) + (\hat{J}_+^2 + \hat{J}_-^2) \hat{J}_z^4 \} \quad (H.22)$$

Expressions for the sextic distortion constants H_J , H_{JK} , H_{KJ} , H_K , h_J , h_{JK} and h_K are given by Aliev and Watson [5].

Appendix I

Vibrational dependence of the rotational constants.

Following Papousek and Aliev [6], the vibrational dependence of the rotational constants is given by

$$B_{\beta}^v = B_{\beta}^e - \sum_k \alpha_k^{\beta} (v_k + \frac{1}{2}) \quad (\text{I.1})$$

where

$$-\alpha_k^{\beta} = \left(\frac{2(B_{\beta}^e)^2}{\omega_k} \right) \left\{ \sum \frac{3(a_k^{\beta\gamma})^2}{4I_{\gamma}^e} + \sum (\zeta_{kl}^{\beta})^2 \frac{3\omega_k^2 + \omega_l^2}{\omega_k^2 - \omega_l^2} + \pi \left(\frac{c}{h} \right)^2 \sum \phi_{kkl} a_l^{\beta\beta} \frac{\omega_k}{\omega_l^{\frac{3}{2}}} \right\} \quad (\text{I.2})$$

(In the case of a strong Fermi resonance ($2\omega_k \sim \omega_l$), Papousek and Aliev suggest the term involving ϕ_{kkl} should be eliminated, but this has not yet been implemented in SPECTRO.)

If there is a Coriolis resonance ($\omega_k \sim \omega_l$), the second term must be replaced by

$$- \sum (\zeta_{kl}^{\beta})^2 \left(\frac{B_{\beta}^e}{\omega_k} \right)^2 \frac{(\omega_k - \omega_l)^2}{\omega_l(\omega_l + \omega_k)} \quad (\text{I.3})$$

and that the resonance itself should be treated by the construction and diagonalization of a matrix of the rotational states of the two coupled vibrations, with

$$\langle v_k, v_l | \widetilde{H} | v_k + 1, v_l - 1 \rangle = i \xi_{vv'}^{\beta} \hat{J}_{\beta} \quad (\text{I.4})$$

$$\xi_{vv'}^{\beta} = 2B_{\beta}^e \zeta_{kl}^{\beta} \left(\left(\frac{\omega_l}{\omega_k} \right)^{\frac{1}{2}} + \left(\frac{\omega_k}{\omega_l} \right)^{\frac{1}{2}} \right) \left(\frac{(v_k + 1)v_l}{4} \right)^{\frac{1}{2}} \quad (\text{I.5})$$

SPECTRO again will issue warnings that there appears to be a resonance, and can do all the replacements and form the matrix elements.

Appendix J

Vibrationally averaged interatomic distances.

It is usual, following Mills [7], to define the average internuclear distance as r_g , and the distance between average nuclear positions as r_α , where

$$r_{ig} = r_{ie} + \sum L_i^r \langle Q_r \rangle + \frac{1}{2} \sum L_i^{ss} \langle Q_s^2 \rangle + \dots \quad (\text{J.1})$$

with

$$\langle Q_r \rangle = - \sum_s \left(\frac{\phi_{rss}}{2\gamma_r^{\frac{1}{2}} \omega_r} \right) \left(v_s + \frac{1}{2} \right) \quad (\text{J.2})$$

$$\langle Q_s^2 \rangle = \gamma_s^{-1} \left(v_s + \frac{1}{2} \right) \quad (\text{J.3})$$

and

$$r_{i\alpha} = r_{ie} + \sum_r L_i^r \langle Q_r \rangle \quad (\text{J.4})$$

where

$$\gamma_r = \frac{2\pi c \omega_r}{\hbar} \quad (\text{J.5})$$

where $\gamma_r^{\frac{1}{2}}$ is the factor used in Appendix F to go from normal coordinates to dimensionless normal coordinates.

Appendix K

Symmetric tops.

A molecule with two equal moments of inertia and one different is called a symmetric top. If the unique moment of inertia is zero then the molecule is linear. All symmetric top molecules have at least a three-fold axis of rotation. Linear molecules belong to the point groups $C_{\infty v}$ or $D_{\infty h}$. Solution of the vibrational problem leads to pairs of normal modes with identical frequencies belonging to the E representation known as degenerate modes. Any linear combination of these modes is itself a normal mode with the same frequency and hence some convention for the modes must be adopted. Normally the degenerate modes are chosen to be symmetric (labelled a) or antisymmetric (labelled b) with respect to a C_2 axis or σ_v plane. The choice is usually dictated by which operation is present in the group. A linear molecule along the z-axis has, by convention, one normal mode in the x direction (a, symmetric) and one in the y direction (b, antisymmetric). For symmetric tops, this alignment is achieved by specifying which atom you wish to put on the x-axis.

The vibrational energy of a symmetric top is of a similar form to that of an asymmetric top except that degenerate modes are treated separately from non-degenerate ones and vibrational angular momentum becomes important. Equation H.1 for asymmetric tops therefore becomes

$$\begin{aligned} E(\mathbf{v}, l) = & \sum_s \omega_s (v_s + \frac{1}{2}) + \sum_t \omega_t (v_t + 1) + \sum_{s \leq s'} x_{ss'} (v_s + \frac{1}{2}) (v_{s'} + \frac{1}{2}) \\ & + \sum_{s,t} x_{st} (v_s + \frac{1}{2}) (v_t + 1) + \sum_{t \leq t'} x_{tt'} (v_t + 1) (v_{t'} + 1) \\ & + \sum_{t \leq t'} g_{tt'} l_t l_{t'} + \dots \end{aligned} \quad (\text{K.1})$$

where s denotes a non-degenerate and t a degenerate mode. The term l_t is the vibrational angular momentum of the degenerate mode t and takes values

$$\pm v_t, \pm(v_t - 2), \dots, 1 \text{ or } 0 \quad (\text{K.2})$$

Extra terms are also introduced into the vibration-rotation interaction due to the degenerate modes. The reader is referred to Ref. 3 for more information. Recently, Pliva [13] has pointed out that the standard formulae for some anharmonic constants omit terms that are non-zero for molecules with four-fold or higher symmetry axes. The new formulae are used if one specifies PLIVA in the Keyword input.

Appendix L

Spherical tops.

A molecule with three equal moments of inertia is called a spherical top. Molecules of this type belong to the cubic symmetry groups T , T_d , O and O_h . We will be primarily interested in those belonging to the T_d group. This high symmetry allows for triply as well as doubly degenerate modes. As with symmetric tops we have to fix the definition of these modes. The usual method is to make two symmetric and one antisymmetric with respect to a σ_d plane.

With the introduction of vibrational angular momentum due to the triply degenerate modes the formulae previously given for asymmetric tops become considerably more complicated. One now has to allow for coupling of this angular momentum with that due to the doubly degenerate modes and the overall angular momentum. At this stage the reader is referred to Ref. 8 and Ref. 9 for more complete treatments. Here we give only a brief introduction. The method found most efficient to handle spherical tops is that of irreducible tensor operators. For example, the transformed rotational Hamiltonian \tilde{H}_{04} is given by

$$\tilde{H}_{04} = -D(\hat{J}^2)^2 - D_t \hat{R}(4) \quad (\text{L.1})$$

where $\hat{R}(4)$ is the irreducible rotational tensor operator of rank 4. Explicitly it is given by

$$\hat{R}(4) = 10 \sum_{\alpha} \hat{J}_{\alpha}^4 - 6(\hat{J}^2)^2 + 2\hat{J}^2 \quad (\text{L.2})$$

The quartic centrifugal distortion constants D and D_t are analogous to those of asymmetric tops. Similarly one obtains the sextic constants H , H_{4t} and H_{6t} from \hat{H}_{06} . The interaction between rotation and vibration is written

$$\tilde{H}_{22} = - \sum_k \alpha_k \left(\frac{1}{2} (q_{t\alpha}^2 + \hat{p}_{t\alpha}^2) \right) \hat{J}^2 + \sum_t \alpha'_t \hat{T}_t(220) + \sum_t \alpha''_t \hat{T}_t(224) + \alpha'_2 \hat{t}_2 \quad (\text{L.3})$$

where $\hat{T}_t(xyz)$ is the vibration-rotation tensor operator derived from $\hat{R}(y)$ and $\hat{V}(x)$. \hat{t}_2 is the operator describing the interaction of the vibrational angular momentum of the doubly degenerate mode and the overall angular momentum. The relationship between the vibration-rotation constants given above and those given by Herranz [9] is

$$\alpha_k = - \left(a_k + \frac{b_k}{3} \right) \quad (\text{L.4})$$

$$\beta_k = \frac{(2b_k + 3c_k)}{15} = \frac{\alpha'_k}{3} \quad (\text{L.5})$$

$$\delta_k = -(b_k - c_k) = -20\alpha''_k \quad (\text{L.6})$$

Turning now to the vibrational Hamiltonian we might expect considerable complication due to the vibrational angular momentum of the degenerate modes. Further, for a molecule of symmetry T_d the energy levels are split into tetrahedral sublevels. The transformed Hamiltonian of interest is \widetilde{H}_{40} given by

$$\widetilde{H}_{40} = \widetilde{H}_{40}(\text{scalar}) + \widetilde{H}_{40}(\text{tensor}) \quad (\text{L.7})$$

The first term gives the anharmonic correction to the vibrational levels analogous to asymmetric top molecules

$$\begin{aligned} \widetilde{H}_{40}(\text{scalar}) = & \sum_{m \leq n} X_{mn} \left(\frac{1}{2} \sum_{\alpha} (q_{m\alpha}^2 + \hat{p}_{m\alpha}^2) \right) \frac{1}{2} \sum_{\beta} (q_{n\beta}^2 + \hat{p}_{n\beta}^2) \\ & + X_{l_2 l_2} \hat{l}_2^2 + \sum_{t \leq t'} X_{l_t l_{t'}} (\hat{l}_t \hat{l}_{t'}) + X'_{34} \hat{V}_{34}(220) \end{aligned} \quad (\text{L.8})$$

where \hat{l}_2 is the vibrational angular momentum operator of the doubly degenerate mode, \hat{l}_t and $\hat{l}_{t'}$ are the corresponding operators for the triply degenerate modes and $\hat{V}_{34}(220)$ is a vibrational irreducible tensor in the space of the triply degenerate modes. The final term is similar to the l-doubling in symmetric tops. These constants can be identified with the notation of Hecht [8]

$$X_{mn} = X_{mn} \quad X_{l_t l_{t'}} = G_{tt'} \quad X'_{34} = S_{tt'} \quad (\text{L.9})$$

The second term in \widetilde{H}_{40} gives the splitting into tetrahedral sublevels

$$\widetilde{H}'_{40} = \sum_{t \leq t'} X''_{tt'} \hat{V}_{tt'}(224) + \sum_t X'_{2t} \hat{V}_{2t}(2) \quad (\text{L.10})$$

As we shall be only be interested in the splitting of the triply degenerate modes we shall ignore the second term. In the notation of Hecht [8]

$$X''_{tt'} = T_{tt'} \quad (\text{L.11})$$

Spherical tops are considerably more complicated than either asymmetric or symmetric tops. As for the symmetric tops described above, the form of the degenerate normal modes must be fixed to convention, but this time the alignment must be performed manually. Any problems with running these molecules should be referred to the authors.

Appendix M

Main Input Options.

Table M.1: Table of input options.

Option	Name	Range of values	Meaning
1	Ncart	1 (or 0) 2 99 5	Cartesian → normal → internal Internal → normal Cartesian → normal Internal → cartesian
2	Isotop	1 (or 0) -1	Use the default weights in subroutine "dist" Use the weights under # WEIGHT #
3	Nbond	#	Number of bond stretches
4	Nbend	#	Number of angle bends
5	Nlbend	#	Number of linear bends
6	Nofpb	#	Number of out-of-plane bends
7	Ntors	#	Number of torsions
8	Nderiv	-2,-3,-4,2, 3 or 4	Highest degree of energy derivative to be used. If negative, read Cartesian second derivatives in HONDO format.
9	Isymm	1 (Yes) 0 (No)	Whether to use internal symmetry coordinates
10	Icurvq	1 (Yes) 0 (No)	Whether to use curvilinear normal coordinates [11], normally 0
11	Idegnl	1 (Yes) 0 (No)	Whether to manually align degenerate normal coordinates normally 0
12	Ifreq	0 (No) # (Yes-number of changes)	Change the labelling of frequencies to match convention
13	Iprnt	0, 1 or 2	Printout options 0 - least output, 2 - most output

Table M.1: Table of input options (continued).

Option	Name	Range of values	Meaning
14	Nwrfq	1 (Yes) 0 (No)	Introduce new harmonic frequencies (Normally 0)
15	Nprop	0, 1, 2, 3	Highest degree of dipole derivative to be used
16	Icoril	0 (No) 1 (Yes) 2 (and change tols)	Account for a Coriolis resonance
17	Iferm1	0 (No) 1 (Yes) 2 (and change tols)	Account for a Fermi type 1 resonance
18	Iferm2	0 (No) 1 (Yes) 2 (and change tols)	Account for a Fermi type 2 resonance
19	Irotrn	0, 1, 2, 3, 4	Project out translation and rotation from cartesian derivatives
20	Ilsqrs	1 (Yes) 0 (No)	Least squares fit harmonic frequencies to observed spectral lines normally 0
21	Iaverg	1 (Yes) 0 (No)	Calculate vibrationally averaged coordinates
22	Irep	0-6	Representation used in computing centrifugal distortion constants (default=0)
23	Iparmf	1 (Yes) 0 (No)	If the force field is restricted or weighted
24	Iparmd	1 (Yes) 0 (No)	If the dipole field is restricted or weighted
25	Igeom	0 1 -1	Read geometry from under # GEOM # Read geometry from unit 10 Read geometry from under # ZMAT #
26	Itemp	#	Temperature to be used in intensity calculations
27	Idarl	0 (Yes) 1 (Yes) 2 (and change tols)	Account for a Darling-Dennison resonance
28	Maxj	#	The maximum value of the angular momentum used in the rotational analysis, normally 0
29	Inorm	0,1,2	Used to read in a new reduced normal coordinate force field. Set to 0.

Appendix N

Input-Output Units.

Table N.1: Table of FORTRAN unit numbers.

Unit Number	Description of use
5	Main Input deck
6	Output
7	Keyword input
8	Print File input
10	Alternative geometry input
15	Cartesian second derivative input
30	Cartesian third derivative input
40	Cartesian fourth derivative input
41	General dump file
51	Coriolis Sum Rule File
55	Reduced normal coordinate third derivative input
56	Reduced normal coordinate fourth derivative input
65	Cartesian equilibrium and first derivative dipole input
66	Cartesian second derivative dipole input
67	Cartesian third derivative dipole input
68	Reduced normal coordinate dipole first derivative input
69	Reduced normal coordinate dipole second derivative input
70	Reduced normal coordinate dipole third derivative input
71	Cartesian first derivative polarisability input
72	Cartesian second derivative polarisability input
75	Cartesian first derivative first hyperpolarisability input

Appendix O

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