User Guide to the *QUAD95* Program

v1.0

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A. Limitations of the current nuclear quadrupole programs

The nuclear quadrupole part of the program suite is limited to the calculation of hyperfine splitting from one quadrupolar nucleus. Both first-order and second-order perturbation methods are available to calculate the hyperfine components. However, only a single cross term of the nuclear quadrupole tensor is currently available in second order. The calculation of hyperfine intensities is based on the *LS*-coupling formalism for spin-orbit coupling in atoms.

B. Generating Nuclear Quadrupole Spectra from the Jb95.exe interface

The first-order nuclear quadrupole spectrum is calculated directly from *jb95.exe*. Hyperfine splitting are calculated from the expectation values of the squared angular momentum components over the rotation wavefunctions generated by *iar95.exe*. As such, off-diagonal quadrupole elements (eQq_{xz}, etc.) are not possible since these expectation values average to zero over the rotational wavefunctions. When the off-diagonal quadrupole tensor element, eQq_{xz}, is important (as might be expected for Cl atom in an planar asymmetric top molecule), then the

second-order program must be used.

To calculate and display the first-order quadrupole spectrum, a rotational spectrum must first be calculated using *iar95.exe* and the simulation read into one of the nine simulation channels. From the SIMULATION CONTROL DIALOG, check the quadrupole trackbar (TB) dialog. The hyperfine components will be calculated and displayed for each rotation transition according to the parameters values in the trackbar dialog. Change the nuclear spin to the desired value. Select the symmetry axis and enter a value for eQq_{zz} (eQq_{zz}, is the component having the largest magnitude and is often coincident or nearly so with a chemical bond axis). The symmetry axis should be defined as the principal axis (*a, b ,c*) that makes the smallest angle with eQq_{zz} tensor component. Adjust the SYM PRM trackbar to automatically define the values of eQq_{yy} and eQq_{xx} or modify the value for one of two parameters directly (see Gordy and Cook, p 254). Note that if the magnitude of eQq*xx* or eQq_{yy} entered is larger than eQq_{zz}, the symmetry axis will automatically be redefined. Refine the magnitude of eQq_{zz} and the symmetry parameter using the trackbars to obtain the best match with the experimental data.

To begin making experimental assignments, check the quadrupole quantum number (QN) dialog box. Double clicking on or near a hyperfine component on the display (or by depressing the CALL button in the QUADRUPOLE QN DIALOG) will select that line's quantum numbers. Notice that the quantum numbers of the associated rotational line(s) will also be displayed and the center frequency of the hyperfine multiplet will be displayed as a vertical line having a label *J* in the center of it. If the multiplet center is not properly located, adjust the *A*, *B*, or *C* rotational constant(s) using the ROTATIONAL CONSTANT TRACKBAR DIALOG (enabled from the SIMULATION CONTROL DIALOG by checking the ABC RIGID box). If Doppler split profiles are present, use the *w*, s and *arrow keys* to adjust the window size to match the Doppler splitting.

The ASSIGN and CLEAR buttons in the QUADRUPOLE QN DIALOG are used to define and clear experimental assignments in memory.

Quadrupole assignments should be saved to file using the WRT ASN button in the Simulation/QUAD PRMS dialog. Prior to writing the file, select from the scrollable list (SIM SEL) the simulation channel containing the assignments. Be sure to click within the box to select it. In general, the proper channel selection must be made prior to performing other operations available in this dialog as discussed below.

To refine the quadrupole parameters and rotational constants, the program *QUAD95.exe* must be run from the 2ND ORDER QUADRUPOLE OPTIONS DIALOG. There is currently no first-order least squares fitting procedure. To define initial values in this dialog, use the IAR->2ND button to copy the rotational constants from the ROTOR OPTIONS DIALOG and the 1ST->2ND button to copy the 1^{ST} order quadrupole parameters. The assignments used in the least squares procedure are read from the file named in the ASN FLNM field. Enter values for the nuclear spin, the maximum *K* to use in the calculation and the number of least square cycles. Check the VAR STAT boxes for those parameters that are to be varied in the least squares fit. Once all parameters have been defined, it is usually a good idea to save these parameters to an INPUT FILE using the WRITE button. Notice that while the input and assignment file used by *IAR95.exe* and *QUAD95.exe* both have ".in" and ".asn" extensions, the ASCII files used by these two programs have different formats. Therefore, be sure to distinguish in the filename the type of file saved.

A least squares analysis using the *QUAD95.exe* program will be performed when the RUN button is pressed. Prior to execution, the user will be prompted with CALC 2ND ORDER FREQS FOR ALL JKK LINES? If answered YES, the program will predict in second order all

hyperfine components of all rotational lines in the simulation. If answered NO, the program will predict only the hyperfine components of the assigned transitions. Note that *QUAD95.exe* is a FORTRAN program (written by Gerald Fraser) and does not dynamically allocate memory. The maximum number of predicted transitions currently allowed is 5000 lines. If an error message is given, try reducing the number of simulated lines using the ITN CUT option in the ROTOR OPTIONS DIALOG.

Once the calculation is finished, an output file named *quad_mod.out* is created and may be read using the RD button. The dialog boxes will be updated with the best fit results and the second-order frequencies will be matched with the corresponding hyperfine transitions defined in first-order. If satisfactory, save the new parameters to the input file and use the 2ND->IAR and 2ND->1ST buttons to update fields in the ROTOR OPTIONS DIALOG and 1ST ORDER QUADRUPOLE TRACKBAR DIALOG. Rerun *IAR95.exe* and update the simulation. The displayed spectrum will be the best representation of the quadrupole spectrum in first order. To display the predicted energies from the 2ND ORDER calculation, check the 2ND ORDER box in the QUADRUPOLE QN DIALOG.

Another useful feature in the 2ND ORDER QUADRUPOLE DIALOG is the button WRT CTR. When pressed, the center frequencies for all quadrupole multiplets having a least one hyperfine component assigned are copied as rotational line assignments to the simulation. These assignments must first be saved to file using the WRITE button in the SIMULATION CONTROL DIALOG if they are to be used by *IAR95.exe* in a least squares fit. This feature is useful when additional Hamiltonian parameters are needed for the calculation of rotational transitions as might be needed for systems having a methyl rotor.

C. Restoring Nuclear Quadrupole spectra from file

The input and assignments files that were saved to disk are the two files needed to restore the quadrupole spectrum upon restarting *JB95.exe*. From the Simulation/QUAD PRMS dialog, first read the quadrupole input file. Select the simulation channel in which to restore the quadrupole parameters and use the 2ND->1ST to restore the quadrupole parameters in the 1^{ST} ORDER QUADRUPOLE DIALOG. Finally, read the assigment file.

Currently, there is only one generic output file called *quad_mod.out* that is created when *QUAD95.exe* is run. This file contains the predicted second-order frequencies. Press the RD button to restore these frequencies to memory. Note, however, that if this *QUAD95.exe* was later used to fit another conformer or isomer, the *quad_mod.out* file will not have the correct second-order frequencies. In this case, rerun *QUAD95.exe* before reading (RD) the *quad_mod.out* file.