# Rotational Hyperfine Structure of $CD_3I$

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The hyperfine structure of the ground state rotational spectrum of $CD_3I$ is remeasured with a greater accuracy and reanalyzed. The determinability of the hyperfine constants is discussed.

## Introduction

The ground state microwave spectrum of $CD_3I$ was first analyzed by Kuczkowski [1]. Later Demaison *et al.* [2] have extended the measurements up to 320 GHz. They have also measured pure quadrupole resonances by laser-radiofrequency double resonance which enabled them to determine with accuracy the quadrupole coupling constant and one spin-rotation constant. They have also been able to point out the effects of the centrifugal distortion on the quadrupole hyperfine structure. Recently the measurements have been extended into the submillimeter region, up to 650 GHz [3] permitting to determine the sextic centrifugal distortion constants $H_J$, $H_{JK}$ and $H_{KJ}$. Parallely to that work, Osipov and Grabois [4] have measured with great accuracy low $J$ quadrupole transitions by microwave-radiofrequency double resonance. The hyperfine constants they have derived are much more accurate than those of [2, 3], but they are also somewhat different. As these authors do not give their frequency measurements, it is not possible to simultaneously fit all the experimental data in order to check the compatibility of the results. To circumvent this difficulty we have remeasured the hyperfine structure of some rotational transitions with an increased accuracy and we have performed a new analysis with emphasis on an accurate determination of the hyperfine constants.

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## Experimental

The sample of $CD_3I$ was purchased commercially from FLUKA A.G. (Buchs, Switzerland) and was used without further purifications.

To determine accurate hyperfine constants it is necessary to measure very accurately the transitions.

Some strong transitions (selection rule: $\Delta F = \Delta J = +1$) have been measured between 60 and 121 GHz with a Lamb dip spectrometer. This spectrometer is similar to a semiconfocal interferometer [5]: the propagation between a plane mirror and a spherical mirror is guided by two parallel plates. The spacing between the plates is 30 mm and the distance between the mirrors is 1 m. The microwave radiation propagates through the cell essentially in the $TE_1$ modes. It is possible to fit the width of these modes between 150 kHz and 1 MHz by adjusting the radius of the spherical mirror. The accuracy of the Lamb dip measurements is thought to be better than 10 kHz.

The $\Delta F = 0$ transitions are much weaker (about 0.2 – 0.1% of the intensity of the $\Delta F = +1$ components) but they are very sensitive to the hyperfine constants. A great number has been measured between 360 and 400 GHz with a source modulation spectrometer using a submillimeter BWO (Thomson) as source. The BWO is phase locked. Its power is optically focused through a free space absorption cell (length: 1 m) and detected by a He cooled InSb bolometer. After phase-sensitive detection, the signal is digitally averaged and processed by a microcomputer (Apple II E) which calculates the line frequency after digital filtering. The accuracy of the measurements is about 100 kHz.

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The other lines have been measured with a computer-controlled mm-wave spectrometer with superheterodyne detection [6]. This spectrometer permits measurements with very low pressure, hence with a good accuracy: between 20 and 50 kHz.

## Theory

The frequency of a rotational transition $J+1, K \leftarrow J, K$ may be written as [7]

$$\begin{aligned} \nu_0 = {} & 2B(J+1) - 4D_J(J+1)^3 \\ & - 2D_{JK}(J+1)K^2 \\ & + H_J(J+1)^3[(J+2)^3 - J^3] \\ & + 4H_{JK}(J+1)^3K^2 \\ & + 2H_{KJ}(J+1)K^4 \ . \end{aligned} \tag{1}$$

The observed transitions exhibit hyperfine structure due to nuclear quadrupole and spin rotation interactions associated with the iodine nucleus in the molecule. These interactions are treated by perturbation theory. The resulting formula for the quadrupole energy is

$$\begin{aligned} E_Q(J,K,F) = {} & \left\{ eqQ_0 \left( \frac{3K^2}{J(J+1)} - 1 \right) \right. \\ & + \chi_J J(J+1) + \chi_{JK} K^2 \\ & \left. + \chi_K \frac{K^4}{J(J+1)} \right\} Y(I,J,F) \\ & + E_Q^{(2)} \frac{(eqQ_0)^2}{B} \\ & + E_Q^{(3)} \frac{(eqQ)^3}{B^2} \ , \end{aligned} \tag{2}$$

where $eqQ_0$ is the quadrupole coupling constant independent of molecular rotation; $\chi_J$, $\chi_{JK}$ and $\chi_K$ are the centrifugal distortion constants introduced by Aliev and Hougen [8]; $Y(I,J,F)$ is Casimir's function, $E_Q^{(2)}$ the coefficient of the second-order contribution, and $E_Q^{(3)}$ this of third-order contribution [9].

The third-order contribution of the quadrupole is significant for several lines and neglecting it gives a definitely worse fit.

The spin-rotation energy is, to first order,

$$\begin{aligned} E_{SR}(J,K,F) = {} & -\frac{1}{2}\left[ C_N + (C_K - C_N)\frac{K^2}{J(J+1)} \right] \\ & \times [F(F+1) - I(I+1) - J(J+1)] \ . \end{aligned} \tag{3}$$

A sign convention consistent with [10] has been used. $C_K$ is the principal value of the spin-rotation tensor along the symmetry axis, and $C_N$ the principal value in the direction perpendicular to it.

## Analysis

The measured transitions are listed in Table 1. First a weighted least-squares method was used to directly fit the frequencies of Table 1 and [1 – 3] to the parameters of (1), (2) and (3). The results of the fit are given in the first column of Table 2. The correlation coefficients are given in Table 3. All the parameters seem well determined. The least well determined constant is $C_K$ for which $C_K/\sigma(C_K) = 5.6$. A statistical $F$-test (test of additional term [11] (see Appendix)) gives a large value for $F_\chi = 31$, so it is clear that the inclusion of $C_K$ improves the fit. However a fit with $C_K$ fixed at the value of Osipov et al. [4] gives a reduced chi-squares $\chi_\nu^2 = 0.472$ identical to the $\chi_\nu^2 = 0.472$ obtained when all the parameters are free. This indicates that the $C_K$ of [4] is probably as good as ours. Our parameter $C_K$ is compatible with the one of [4] within one standard deviation. The contribution of $C_K$ to the frequencies is greater than 50 kHz for only 15 lines, and it is never greater than 100 kHz. As our best experimental accuracy is 10 kHz, this shows that only the order of magnitude of $C_K$ may be determined. After $C_K$, the least well determined parameter is $\chi_K$ for which $\chi_K/\sigma(\chi_K) = 9.2$. But the contribution of $\chi_K$ to the frequencies is greater than 50 kHz for 28 lines and is greater than 100 kHz for still 8 lines. So it may be concluded that $\chi_K$ is slightly better determined than $C_K$.

On the other hand the constants $\chi_J$ and $\chi_{JK}$ seem to be incompatible. Indeed a fit with the hyperfine constants $C_N$, $C_K$, $\chi_J$, $\chi_{JK}$ and $\chi_K$ fixed at the values of [4] (last column of Table 2) is worse ($\chi_\nu^2 = 0.613$ instead of 0.472). But the residues of only a few lines grow significantly. Although these

Table 1. Newly measured transitions of $CD_3I$ (in MHz). To calculate the frequencies the constants of first column of Table 2 were used.

| $J$ | $K$ | $2F''$ | $2F'$ | exp. | e.-c. | $J$ | $K$ | $2F''$ | $2F'$ | exp. | e.-c. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 0 | 13 | 15 | 60411.371 | 0.016 | 9 | 8 | 21 | 23 | 120682.683 | 0.020 |
| 4 | 0 | 11 | 13 | 60419.447 | 0.013 | 9 | 8 | 17 | 19 | 120674.647 | 0.018 |
| 4 | 0 | 9 | 11 | 60396.072 | 0.017 | 9 | 8 | 13 | 15 | 120842.868 | −0.006 |
| 4 | 0 | 7 | 9 | 60369.688 | 0.003 | 9 | 9 | 21 | 23 | 120652.812 | −0.006 |
| 4 | 0 | 5 | 7 | 60359.724 | 0.041 | 9 | 9 | 17 | 19 | 120644.970 | 0.021 |
| 4 | 0 | 3 | 5 | 60378.142 | 0.025 | 9 | 9 | 13 | 15 | 120858.139 | 0.021 |
| 4 | 1 | 13 | 15 | 60418.770 | −0.024 | 29 | 0 | 59 | 59 | 362034.581 | −0.001 |
| 4 | 1 | 11 | 13 | 60408.554 | 0.035 | 29 | 0 | 55 | 55 | 362294.090 | −0.043 |
| 4 | 1 | 9 | 11 | 60385.826 | 0.007 | 29 | 1 | 57 | 57 | 362167.703 | −0.042 |
| 4 | 1 | 7 | 9 | 60368.738 | 0.012 | 29 | 2 | 59 | 59 | 362022.704 | −0.131 |
| 4 | 1 | 5 | 7 | 60370.136 | 0.019 | 29 | 2 | 55 | 55 | 362278.849 | 0.029 |
| 4 | 1 | 3 | 5 | 60397.056 | −0.007 | 29 | 3 | 55 | 55 | 362259.895 | 0.024 |
| 9 | 0 | 21 | 23 | 120796.518 | −0.007 | 29 | 4 | 57 | 57 | 362116.127 | 0.031 |
| 9 | 1 | 19 | 21 | 120789.689 | −0.005 | 29 | 5 | 61 | 61 | 361821.327 | 0.044 |
| 9 | 1 | 15 | 17 | 120782.365 | 0.010 | 29 | 5 | 57 | 57 | 362085.277 | −0.008 |
| 9 | 1 | 13 | 15 | 120787.419 | −0.011 | 29 | 6 | 63 | 63 | 361649.094 | 0.063 |
| 9 | 2 | 23 | 25 | 120794.998 | −0.025 | 29 | 6 | 59 | 59 | 361926.509 | 0.082 |
| 9 | 2 | 21 | 23 | 120789.344 | −0.004 | 29 | 7 | 63 | 63 | 361624.700 | 0.054 |
| 9 | 2 | 19 | 21 | 120782.847 | 0.008 | 29 | 7 | 59 | 59 | 361887.630 | 0.005 |
| 9 | 2 | 17 | 19 | 120779.051 | −0.043 | 29 | 8 | 59 | 59 | 361842.596 | 0.116 |
| 9 | 2 | 15 | 17 | 120780.663 | −0.006 | 29 | 8 | 55 | 55 | 362051.674 | −0.119 |
| 9 | 3 | 23 | 25 | 120796.042 | −0.014 | 29 | 9 | 61 | 61 | 361682.429 | 0.020 |
| 9 | 4 | 23 | 25 | 120797.500 | −0.001 | 29 | 10 | 61 | 61 | 361635.432 | −0.027 |
| 9 | 4 | 21 | 23 | 120767.872 | 0.001 | 29 | 11 | 57 | 57 | 361756.377 | 0.003 |
| 9 | 4 | 19 | 21 | 120755.531 | 0.010 | 29 | 12 | 55 | 55 | 361749.099 | −0.020 |
| 9 | 4 | 17 | 19 | 120758.176 | 0.012 | 29 | 14 | 61 | 61 | 361398.439 | −0.023 |
| 9 | 4 | 13 | 15 | 120800.454 | −0.020 | 29 | 14 | 55 | 55 | 361552.889 | −0.039 |
| 9 | 5 | 23 | 25 | 120799.373 | 0.002 | 29 | 15 | 57 | 57 | 361401.421 | −0.111 |
| 9 | 5 | 21 | 23 | 120751.817 | 0.001 | 29 | 17 | 61 | 63 | 361179.830 | 0.089 |
| 9 | 5 | 19 | 21 | 120735.077 | −0.019 | 29 | 17 | 57 | 59 | 361172.582 | 0.018 |
| 9 | 5 | 17 | 19 | 120742.538 | 0.018 | 29 | 17 | 53 | 55 | 361200.596 | 0.005 |
| 9 | 5 | 15 | 17 | 120768.651 | 0.000 | 29 | 18 | 61 | 63 | 361079.279 | 0.038 |
| 9 | 5 | 13 | 15 | 120808.334 | −0.031 | 29 | 18 | 53 | 55 | 361102.710 | −0.062 |
| 9 | 6 | 23 | 25 | 120801.652 | −0.005 | 29 | 19 | 53 | 55 | 360999.266 | −0.004 |
| 9 | 6 | 21 | 23 | 120732.243 | 0.006 | 29 | 21 | 59 | 61 | 360731.308 | −0.004 |
| 9 | 6 | 19 | 21 | 120710.019 | 0.009 | 29 | 21 | 53 | 55 | 360776.307 | −0.006 |
| 9 | 6 | 17 | 19 | 120723.433 | 0.000 | 29 | 24 | 53 | 55 | 360401.854 | −0.007 |
| 9 | 6 | 15 | 17 | 120762.371 | 0.004 | 32 | 12 | 63 | 63 | 397758.085 | 0.030 |
| 9 | 7 | 23 | 25 | 120804.327 | −0.024 | 32 | 13 | 69 | 71 | 397595.127 | −0.115 |
| 9 | 7 | 21 | 23 | 120709.178 | 0.020 | 32 | 14 | 69 | 69 | 397367.872 | −0.053 |
| 9 | 7 | 17 | 19 | 120700.784 | 0.023 | 32 | 15 | 69 | 69 | 397300.492 | −0.036 |
| 9 | 7 | 13 | 15 | 120829.527 | −0.045 | 32 | 15 | 61 | 61 | 397522.656 | 0.082 |
| | | | | | | 32 | 17 | 63 | 63 | 397236.604 | 0.020 |

Table 2. Molecular constants of $CD_3I$ – $\chi^2_v$: reduced chi-square. Standard errors in units of the last digit in brackets.

| | Fit of the frequencies | | Jackknife | | Fit of the splittings | | Other works | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| $B$ [MHz] | 6040.297657 | (114) | 6040.297730 | (126) | | | 6040.29728 | (38) | [3] |
| $D_J$ [kHz] | 3.722160 | (185) | 3.722127 | (225) | | | 3.72188 | (30) | [3] |
| $D_{JK}$ [kHz] | 48.29460 | (133) | 48.29456 | (133) | | | 48.2963 | (36) | [3] |
| $H_J$ [Hz] | −0.001469 | (48) | −0.001481 | (69) | | | −0.001530 | (60) | [3] |
| $H_{JK}$ [Hz] | 0.03225 | (91) | 0.03224 | (84) | | | 0.03775 | (192) | [3] |
| $H_{KJ}$ [Hz] | 1.0202 | (36) | 1.0200 | (34) | | | 1.0080 | (63) | [3] |
| $eqQ_0$ [MHz] | −1928.983 | (38) | −1928.984 | (46) | −1928.973 | (36) | −1928.9660 | (27) | [4] |
| $\chi_J$ [kHz] | 0.938 | (140) | 0.933 | (130) | 1.241 | (169) | 2.19 | (48) | [4] |
| $\chi_{JK}$ [kHz] | 30.51 | (122) | 30.47 | (109) | 29.23 | (137) | 23.07 | | [4] |
| $\chi_K$ [kHz] | −22.0 | (24) | −21.80 | (20) | −24.3 | (26) | −14.3 | | [4] |
| $C_N$ [kHz] | −14.34 | (32) | −14.36 | (37) | −14.32 | (46) | −14.06 | (19) | [4] |
| $C_K$ [kHz] | −10.64 | (190) | −10.67 | (186) | −11.1 | (26) | −8.64 | (11) | [4] |
| Number of data | 301 | | 301 | | 191 | | | | |
| $\chi^2_v$ | 0.472 | | | | 0.388 | | | | |

Table 3. Correlation coefficients.

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Fit of the frequencies* | | | | | | | | | | | | |
| $B$ | 1.000 | | | | | | | | | | | |
| $D_J$ | 0.686 | 1.000 | | | | | | | | | | |
| $D_{JK}$ | 0.392 | −0.056 | 1.000 | | | | | | | | | |
| $H_J$ | 0.581 | 0.961 | −0.117 | 1.000 | | | | | | | | |
| $H_{JK}$ | 0.359 | 0.436 | 0.325 | 0.363 | 1.000 | | | | | | | |
| $H_{KJ}$ | 0.077 | −0.252 | 0.584 | −0.245 | −0.510 | 1.000 | | | | | | |
| $eqQ_0$ | −0.022 | −0.011 | −0.006 | −0.010 | 0.011 | −0.022 | 1.000 | | | | | |
| $C_N$ | 0.165 | 0.345 | −0.112 | 0.330 | −0.110 | 0.069 | 0.011 | 1.000 | | | | |
| $C_K$ | 0.069 | 0.052 | 0.121 | 0.050 | −0.245 | 0.317 | −0.019 | −0.058 | 1.000 | | | |
| $\chi_J$ | 0.016 | 0.116 | −0.045 | 0.114 | 0.072 | −0.068 | 0.292 | −0.097 | 0.063 | 1.000 | | |
| $\chi_{JK}$ | −0.007 | −0.080 | 0.055 | −0.081 | −0.003 | 0.010 | 0.011 | 0.095 | −0108 | −0.738 | 1.000 | |
| $\chi_K$ | −0.015 | −0.009 | −0.054 | −0.003 | −0.146 | 0.119 | −0.261 | −0.080 | 0.203 | 0.144 | −0.490 | 1.000 |
| *Fit of the splittings* | | | | | | | | | | | | |
| $eqQ_0$ | 1.000 | | | | | | | | | | | |
| $C_N$ | 0.009 | 1.000 | | | | | | | | | | |
| $C_K$ | 0.005 | 0.317 | 1.000 | | | | | | | | | |
| $\chi_J$ | 0.226 | 0.093 | 0.078 | 1.000 | | | | | | | | |
| $\chi_{JK}$ | 0.004 | −0.035 | −0.041 | −0.776 | 1.000 | | | | | | | |
| $\chi_K$ | −0.252 | 0.018 | 0.113 | 0.194 | −0.517 | 1.000 | | | | | | |

lines are the most sensitive to the hyperfine constants, their residues are still lower than $3\sigma$. So it is very difficult to draw any conclusion.

It is interesting to determine the parameters and their standard deviations by an independent method in order to check the validity of the results. We have used the jackknife technique [12–14] which seems well appropriate to our problem: The vector representing the unknown parameters may be written

$$x = f(y_1, y_2, \ldots, y_n) \ , \tag{4}$$

where the $y_i$ are the measurements (frequencies) supposed to form a sample of independent and identically distributed random variables. Let $\hat{x}$ be an estimator of $x$ based on the whole sample. The jackknife estimate is computed by dropping one of the measurements to give partial estimates:

$$\begin{aligned} \hat{x}_{-1} &= f(y_2, y_3, \ldots, y_n) \ , \\ \hat{x}_{-2} &= f(y_1, y_3, \ldots, y_n) \ , \\ &\ldots\ldots\ldots\ldots\ldots \\ \hat{x}_{-n} &= f(y_1, y_2, \ldots, y_{n-1}) \ . \end{aligned} \tag{5}$$

$$\text{Define } \hat{x}_i = m\hat{x} - (n-1)\hat{x}_{-i} \ (i = 1, \ldots, n) \ . \tag{6}$$

The jackknife estimate of $x$ is

$$\tilde{x} = \frac{1}{n} \sum_{i=1}^{n} \hat{x}_i = n\hat{x} - \frac{(n-1)}{n} \sum_{i=1}^{n} \hat{x}_{-i} \ , \tag{7}$$

and the corresponding variance is

$$\sigma^2 = \sum_{i=1}^{n} \frac{(\hat{x}_{-i} - \tilde{x})^2}{n(n-1)} \ . \tag{8}$$

The drawback of this method is that it is very expensive in computer time. But in our particular case, although we have 301 data and 12 parameters, it is still acceptable: about 4 hours on a Macintosh + for a program written in FORTRAN (instead of 2 mn for the direct least-squares fit). The results are given in the second column of Table 2. It may be seen that the agreement is very good with the ordinary least-squares method.

The determination of the hyperfine parameters from a direct fit of the rotational transitions may be strongly affected by small systematic error measurements because the hyperfine contributions to the rotational frequency is only a small percentage of the frequency. To eliminate at least partially these errors it is possible to use the splittings between frequencies of hyperfine multiplets as input in the least-squares analysis. In this case the data are no more statistically independent but are correlated. The neglect of these correlations can lead to constants differing significantly from those obtained by the correct procedure and can also underestimate the rms errors of those constants [15]. Lees [16] has shown how the least-squares procedure should be modified: the diagonal weight matrix in the weighted least-squares procedure has to be replaced by a nondiagonal matrix $\tilde{V}^{-1}$, where $\tilde{V}$ is the variance-covariance matrix for the

data. The form of $\tilde{V}$ depends on the choice of observable. The easiest procedure is to take the strongest component of each multiplet as the reference line $\nu_0$, and take the differences between all other components and the reference as observables $y_i = \nu_i - \nu_0$. The variance-covariance matrix $\tilde{V}$ is then block-diagonal, with a block associated with each multiplet. Its elements are

$$V_{ij} = \begin{cases} 2\sigma^2 , & i = j \\ \sigma^2 , & i \neq j , \end{cases}$$

where $\sigma^2$ is the variance of $\nu_i$ and $\nu_0$. It is to be noted that different multiplets may have different variances. $\tilde{V}^{-1}$ has a very simple form which is very easy to calculate [16]. On the other hand if the individual lines of a multiplet have different measurement accuracies, the $\tilde{V}$ matrix has to be inverted numerically. But this complex procedure was unnecessary in our case. The results of the correlated least-squares procedure are shown in the third column of Table 2 and the correlation coefficients in Table 3. The results are in very good agreement with those of the first two columns of Table 2, but the standard deviations are slightly higher. It could be simply due to the fact that the number of degrees of freedom is smaller: 191 data for 6 parameters versus, 301 data for 12 parameters in the first two cases. In fact if we randomly drop some data in the fit of the frequencies, the standard deviations increase too. Moreover if we correct the frequencies for the hyperfine interactions and then fit the unperturbed frequencies to the six parameters of (1), we get also higher standard deviations than those of the first column of Table 2 although we are sure in this case not to lose any information. But here again the numbers of degrees of freedom is smaller: 99 data for 6 parameters. As expected, neglecting the correlations between the experimental data increases significantly the standard deviation of the fit (26 kHz instead of 20 kHz) and modifies the values of some parameters.

The $eqQ_0$ of Osipov and Grabois [4] is more accurate than ours. It is not surprising because these authors have accurately measured pure quadrupole transitions of low $J$, these transitions being the most sensitive to $eqQ_0$. Their $C_N$ and $C_K$ are more accurate too. This may also be due to the great accuracy of their measurements. It is to be noted that their $eqQ_0$, $C_N$ and $C_K$ are compatible with ours within one standard deviation. On the other hand their centrifugal constants $\chi_J$, $\chi_{JK}$ and $\chi_K$ are different from ours. But their greatest $J$ value was only 7 whereas ours is 32 and our greatest $K$ value is 24, so our centrifugal constants are very likely better determined: for instance the maximum contribution of $\chi_J$ to the quadrupole transitions $J = 7$ is only 9 kHz (19/2 – 17/2 component) whereas this contribution is greater than 100 kHz for 26 of our rotational transitions (and greater than 150 kHz for 8 rotational transitions).

## Conclusion

The rotational hyperfine structure of $CD_3I$ in this vibrational ground state has been analyzed by three different methods. They give results in very good agreement. So it may be concluded that the derived parameters are reliable, although some of them ($C_K$ and $\chi_K$) are not very accurate. Their accuracy could be improved by using pure quadrupole transitions, like those measured by Osipov and Grabois [4].

## Appendix

We have $n$ measurements $y_i$ of standard deviation $\sigma_i$ to be fitted to $p$ parameters $x_i$. The column vectors $x$ and $y$ are related by the matrix equation [17]

$$y = Ax .$$

The solution is

$$x = (\tilde{A}\,WA)^{-1}\tilde{A}\,Wy ,$$

where $\tilde{A}$ is the transpose of $A$ and $W$ the weight matrix, with

$$W_{ij} = \sigma_{ij}\frac{1/\sigma_i^2}{(1/n)\,\Sigma(1/\sigma_i)} .$$

The $\chi^2$ of the fit is [10]

$$\chi^2 = \sum_{i=1}^{n}\frac{\Delta y_i^2}{\sigma_i^2} , \quad \text{where} \quad y_i = y_i^{\text{exp}} - y_i^{\text{calc}} ,$$

and the reduced $-\chi^2$

$$\chi_\nu^2 = \frac{\chi^2}{n-p-1} .$$

If the model is appropriate for describing the data, than $\chi^2_\nu \sim 1$.

The formula for $F_\chi$ is

$$F_\chi = \frac{\chi^2(p-1) - \chi^2(p)}{\chi^2_\nu(p)} \ .$$

$F_\chi$ follows the $F$ distribution and should be small when the model with $p$ terms does not significantly improve the fit over the model with $p-1$ terms.

When the observables are correlated, the weight matrix $W$ has simply to be replaced by the inverse $\tilde{V}^{-1}$ of the variance-covariance matrix $V$ [15]. These two matrices are block-diagonal, with a block of the form

$$V = \sigma^2 \begin{pmatrix} 2 & 1 & 1 & \dots & 1 \\ 1 & 2 & 1 & \dots & 1 \\ \vdots & & & & \vdots \\ 1 & 1 & 1 & \dots & 2 \end{pmatrix} ,$$

$$V^{-1} = \frac{1}{\sigma^2(n+1)} \begin{pmatrix} n & -1 & \dots & -1 \\ -1 & n & & -1 \\ \vdots & & & \vdots \\ -1 & -1 & -1 & n \end{pmatrix} .$$


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