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Citation: *The Journal of Chemical Physics* **86**, 4725 (1987); doi: 10.1063/1.452692

View online: <http://dx.doi.org/10.1063/1.452692>

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# Quadrupole structure in the rotational spectrum of the $\nu_8 = 1$ and 2 and ground vibrational levels of $\text{CH}_3\text{C}^{14}\text{N}$ for the frequency range 17–56 GHz<sup>a)</sup>

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(Received 1 October 1986; accepted 12 January 1987)

The rotational spectra in the ground and  $\nu_8 = 1$  and 2 vibrational states of methyl cyanide have been determined in the frequency range 17–56 GHz. Molecular constants for these vibrationally excited states have been determined from more than 30 observed rotational transitions. Experimentally measured frequencies are presented and compared with those calculated using the results of basic perturbation theory. Constants were obtained for the  $\nu_8 = 1$  level and these, along with the ground constants, used to generate constants for components of the  $\nu_8 = 2$  vibration. A model was developed for the quadrupole splitting for the ground and  $\nu_8 = 1$  levels. From these values spectral components were predicted and assigned for the higher vibration  $\nu_8 = 2$ .

## I. INTRODUCTION

Several papers dealing with the structure of the methyl cyanide molecule in its ground and vibrationally excited states have appeared over the last few years.<sup>1–7</sup> This investigation deals with the structural pattern of  $\text{CH}_3\text{C}^{14}\text{N}$  when it is excited to the  $\nu_8 = 1$  and higher levels. The observed spectrum in the  $\nu_8$  levels was found to be very weak compared to the ground. For the  $\nu_8 = 3$  levels the intensity was estimated to be < 1% of the ground population. Moreover, a number of degeneracies have been removed with respect to the quantum number  $l$  producing further redistribution of the spectral line intensity.

We have extended our earlier work<sup>8–11</sup> on the ground,  $\nu_9 = 1$ , and  $\nu_{10} = 1, 2, 3$ , and 4 states of propyne another  $\text{C}_{3v}$  symmetry molecule, to compare these results with some components in the methyl cyanide molecule. The data obtained by us for the lower vibrations have made it possible to predict properties up to the  $\nu_{10} = 4$  vibrational manifolds very accurately. Frequency components could be expressed to within a few hundred kHz using the molecular parameters which were derived from lower states and refined using a computer iterative technique.<sup>11</sup>

The general patterns for the values of  $q_{12}$ ,  $d_{12}$ , and  $x_{11}$  which were found for the  $\nu_{10}$  vibrations in the propyne molecule were used to generate trial constants to begin the assignment of the  $\nu_8$  components in the  $\text{CH}_3\text{C}^{14}\text{N}$  molecule. These patterns were, however, found to be more complicated in the  $\text{CH}_3\text{C}^{14}\text{N}$  than in propyne due to quadrupole splitting.

Spectral components were identified and their frequencies measured to accuracies of better than 200 kHz. The components which have been assigned and are given in Tables I–II of PAPS.<sup>12</sup> A summary of the molecular constants obtained for the rotational energy levels of the  $\nu_8$  vibrational states is given in Table I of this work. Some of the constants for the  $\nu_8 = 1$  and  $\nu_8 = 2$  levels were taken from Boucher *et al.*<sup>13</sup> and Bauer,<sup>2</sup> respectively.

## II. EXPERIMENTAL APPARATUS

The measurements reported in this work were made using the same spectrometer as described earlier.<sup>8</sup> The sensitivity of the instrument has been made quite high using a cylindrical cell of 47 m length. The cell was excited by a rectangular to circular feed horn and detection achieved reciprocally.

The spectral line profiles were displayed on a dual trace recorder with one pen producing the frequency markers and the other pen producing the spectral line profiles. Figure 1 shows a scan of the  $\Delta J = 3 - 2$  rotational transition of the  $\nu_8 = 2$  vibrational state with the background scan and the absorption spectrum both shown. These background signals, although very weak, were comparable to some of the weaker signals observed. For these components resolution became difficult and a series of runs had to be made to pressurize and depressurize the cell with a gas sample until the resonance profile could be identified.

TABLE I. Rotational constants for  $\text{CH}_3\text{C}^{14}\text{N}$  in the ground,  $\nu_8 = 1$ , and  $\nu_8 = 2$  excited vibrational states.

	Ground	$\nu_8 = 1$	$\nu_8 = 2$
$eqQ$	− 4.546 67	− 3.991 11	− 3.480 56
$C_N$	− 0.012 00	− 0.010 335	0.005 58
$C_K$	− 0.000 7	− 0.000 7	− 0.000 7
$\eta$		− 0.026 15	
$B_V$	9198.930 41	9 226.341 65	9 252.808 6
$A$		157 300	152 400
$D_J$	0.015 031	0.003 886	0.004
$D_{JK}$	0.162 5525	0.177 972	0.178 3
$\xi$		0.877	0.872
$x_{11}$		167 800	162 975
$q_0$		4.453 1	4.482
$\eta_J$		0.388 7	0.392 9
$\gamma_{11}$		0.105 44	0.106 9
$q_{12}$		0.0	0.0
$d_{12}$		0.0	0.0
$\eta_{JJ}$		0.0	0.0
$\eta_{JK}$		0.0	0.0

<sup>a)</sup> This work supported by Grant No. B842 from the Robert A. Welch Foundation.

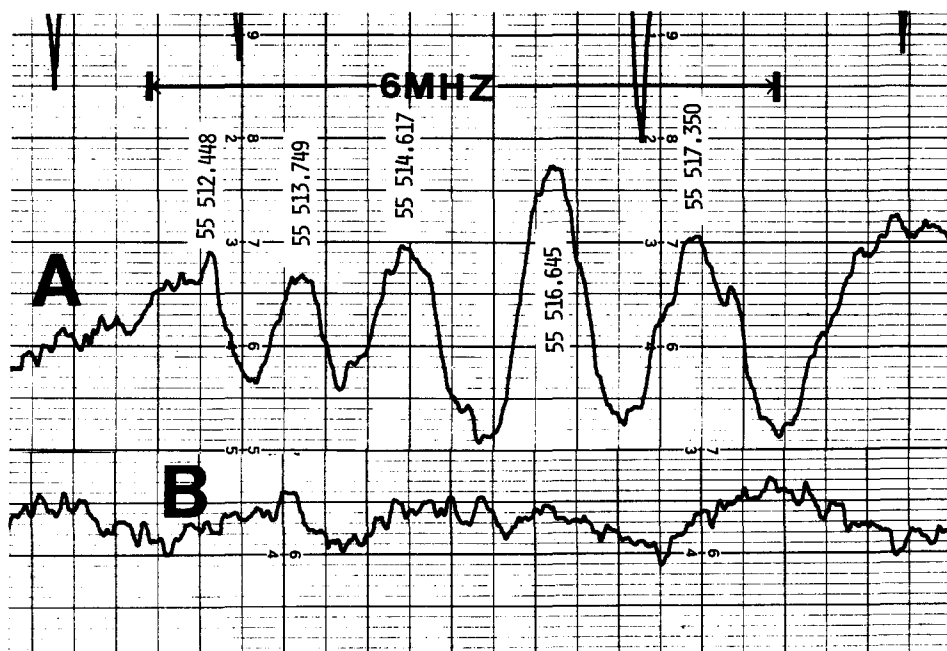


FIG. 1. Chart recorder scan of the  $\Delta J = 3 \leftarrow 2$  rotational transition of the  $\nu_8 = 2$  vibrational state of  $\text{CH}_3\text{C}^{14}\text{N}$ . A is the spectral scan and B the background profile.

### III. DISCUSSION

As can be seen from the equation given in the Appendix, the least deviation is expected for the  $l = K = 0$  components in each  $J$  level. Experimental values can be taken from these transitions, once they are assigned, to best express the rotational constants for a given vibrational state. Refinements are then made for the  $K$  and  $l$  branching of each  $J$  level with relative shifts in frequency from the above components as reference. "Constants" appearing in each perturbation term could be expressed in a power series in the quantum number  $v$  as they were found not to vary much over the low  $J$  energy levels.

Some constants obtained from lower vibrations were used to make estimates for the constants of the higher vibrations. To get remaining constants, more tentative assignments were made following a procedure suggested by Bauer *et al.*<sup>14</sup> For  $K = 0$ , the general equations derived from perturbational procedures can be extended and expressed in the following way for a specific vibrational state containing hyperfine splitting: (See the Appendix and Ref. 10.)

$$\begin{aligned} \nu(J, K=0, l=\text{even}) \\ (J+1) \\ = I_e + M_e(J+1)^2 + \Delta\nu_e + \Delta\nu(\text{hfs}) \end{aligned} \quad (1)$$

for even values of  $l$  and

$$\begin{aligned} \nu(J, K=0, l=\text{odd}) \\ (J+1) \\ = I_0 + M_0(J+1)^2 + \Delta\nu_0 + \Delta\nu(\text{hfs}) \end{aligned} \quad (2)$$

for odd values of  $l$ .

Where the parameters  $I_0$ ,  $M_0$ ,  $I_e$ , and  $M_e$  are coefficients arising from the perturbational procedure employed. In each case  $\Delta\nu_i$  is small and including these terms changes the results in most frequencies by only a few kHz. The  $\Delta\nu_i$  terms arise when  $q_0$  is replaced by  $q_v = q_0 + f_{22}^J J(J+1) + \dots$  in

the general equation derived from second order perturbation (Appendix) and in the equation given by Bauer and Gordon.<sup>15</sup>

The frequency equations given above have been modified to take into account the hyperfine splitting due to the  $^{14}\text{N}$  nucleus. The modified frequency terms are obtained by using the appropriate selection rules and a table of Casimir functions.<sup>16</sup> The  $J = 1 \leftarrow 0$  transition for the  $\nu_8 = 3$  set was too weak to be satisfactorily resolved with our spectrometer.

Once identification of components of major branches was made, the constants for other branches were approximated and refined by iterative techniques.

The trial set of constants obtained as above was further refined in successive iterations based on the least squares method in order to get the best overall agreement with all the experimental data for the measurements. Systematic departures between experiment and theory were studied to determine additional procedures to be used for refining the calculations.

The presence of quadrupole splitting in the  $\text{CH}_3\text{C}^{14}\text{N}$  spectrum produces some ambiguities in frequency assignment but not in quantum number assignment as each set of hyperfine components retained their relative positions in the ground and higher vibrational states. The assignments given in Tables I–III are measured to accuracies of better than 200 kHz.<sup>12</sup> The value of the  $eqQ$  presented is that for which a maximum number hyperfine components can be predicted.

The results obtained on the  $\nu_8 = 1$  and 2 and ground rotational components of  $\text{CH}_3\text{C}^{14}\text{N}$  have enabled a very accurate model to be formulated for the  $\nu_8$  vibrations in the presence of hyperfine structure. Intensity estimates, based on the  $\nu_8 = 1$  and  $\nu_8 = 2$  components observed, indicate that extreme difficulty will be encountered in observing higher vibrations for these low  $J$  numbers due to reduced intensity by hyperfine splitting.

A preliminary study of the spectrum of  $\text{CH}_3\text{C}^{15}\text{N}$  indi-

cates that our model for CH<sub>3</sub>C<sup>14</sup>N can be used to predict a very accurate set of spectral components for CH<sub>3</sub>C<sup>15</sup>N by suppressing the hyperfine terms in the general equation of frequency for the CH<sub>3</sub>C<sup>14</sup>N components. The frequency components appear to be stronger in the CH<sub>3</sub>C<sup>15</sup>N spectrum than in the CH<sub>3</sub>C<sup>14</sup>N spectrum due to quadrupole splitting.

Since the pattern for CH<sub>3</sub>C<sup>15</sup>N and CH<sub>3</sub>C<sup>14</sup>N should be the same, except for the quadrupole splitting in the CH<sub>3</sub>C<sup>14</sup>N, we expect to produce a more complete model of the acetonitrile spectrum when our study on CH<sub>3</sub>C<sup>15</sup>N has been completed.

#### APPENDIX: DERIVATION OF A GENERAL FREQUENCY EQUATION FOR C<sub>3v</sub>-TYPE MOLECULES

To derive this model, we used the diagonal and nondiagonal matrix element of the Hamiltonian for a C<sub>3v</sub> molecule

$$E^{(1)} = X_{II}l^2 + B_vJ(J+1) + \gamma_{II}l^2J(J+1) + (A-B)_vK^2 + (A_3-B_3)l^2K^2 - 2(A\zeta)_vKl - 2(A\zeta)_3Kl^3 - D_JJ^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_KK^4 + \eta_JJ(J+1)Kl + \eta_KK^3l + \eta_{JJ}J^2(J+1)^2Kl + \eta_{JK}J(J+1)K^3l + \eta_{KK}K^5l + H_JJ^3(J+1)^3 + H_{JJK}J^2K^2 + H_{JKK}J(J+1)K^4 + H_{KK}K^6, \quad (A2)$$

where  $B_v, A_v$ : Rotational constants.

$x_{II}$ : Anharmonic constant.

$\zeta$ : Coriolis coupling constant.

$D_J, D_{JK}, D_K$ : First order centrifugal distortion constants.

$H_J, H_{JJK}, H_{JKK}, H_K$ : Higher order centrifugal distortion constants.

$B_3 = \gamma_{II}$ .

$\eta_J, \eta_{JJ}, \eta_{JK}, \eta_{KK}$ : Higher order diagonal matrix elements.

For the second order energy correction, three major nondiagonal Hamiltonian matrix elements:  $(K, l|H'|K \pm 2, l \pm 2)$ ,  $(K, l|H'|K \pm 1, l \mp 2)$ , and  $(K, l|H'|K \pm 2, l \mp 4)$  were used. The second order energy is given by

$$E^{(2)} = \frac{[q_{12}(2K+1) + d_{12}(l-1)]^2(a_1^+b_2^-)^2}{H'_{\omega K l} - H'_{\omega K + 1l - 2}} + \frac{[q_{12}(2K-1) + d_{12}(l+1)]^2(a_1^-b_2^+)^2}{H'_{\omega K l} - H'_{\omega K - 1l + 2}} + \frac{(q_v a_2^+ b_2^+)^2}{H'_{\omega K l} - H'_{\omega K + 2l + 2}} + \frac{(q_v a_2^- b_2^-)^2}{H'_{\omega K l} - H'_{\omega K - 2l - 2}} + \frac{(f_{24} a_2^+ b_4^-)^2}{H'_{\omega K l} - H'_{\omega K + 2l - 4}} + \frac{(f_{24} a_2^- b_4^+)^2}{H'_{\omega K l} - H'_{\omega K - 2l + 4}}, \quad (A3)$$

where

$H'_{\omega K} = [vJK|H'|vJK]$ , etc.,

$a_1^\pm = [J(J+1) - K(K \pm 1)]^{1/2}$ ,

$a_2^\pm = [J(J+1) - K(K \pm 1)]^{1/2}[J(J+1) - (K \pm 1)(K \pm 2)]^{1/2}$ ,

$b_1^\pm = [(v+l+1 \pm 1)(v-l+1 \mp 1)]^{1/2}$ ,

$b_2^\pm = [(v+l+1 \pm 1)(v-l+1 \mp 1)(v+l+1 \pm 3)(v-l+1 \mp 3)]^{1/2}$ .

To calculate the energy difference which appears in the denominator of  $E^{(2)}$ , some small terms, i.e.,  $A_3$ ,  $(B_3 = \gamma_{II})$ ,  $(A\zeta)_3$ ,  $D_{JK}^v$ ,  $D_K^v$ ,  $D_J^v$ ,  $\eta_J$ ,  $\eta_{JJ}$ ,  $\eta_{JK}$ ,  $\eta_{KK}$ ,  $H_J$ ,  $H_{JJK}$ ,  $H_{JKK}$ ,  $H_K$  were ignored, since these terms are very small compared to  $A_v$ ,  $B_v$ ,  $X_{II}$ ,  $(A\zeta)_v$ . (See Ref. 9 for identification of the terms.)

Therefore, the energy difference terms are simplified to

$$\begin{aligned} H'_{\omega K l} - H'_{\omega K + 1l - 2} &= X_{II}[l^2 - (l-2)^2] + (A-B)[K^2 - (K+1)^2] \\ &\quad - 2(A\zeta)[Kl - (K+1)(l-2)] = 4X_{II}(l-1) - (A-B)(2K+1) - 2A\zeta(2K-l+2), \\ H'_{\omega K l} - H'_{\omega K - 1l + 2} &= -4X_{II}(l+1) + (A-B)(2K-1) - 2A\zeta(-2K+l+2), \\ H'_{\omega K l} - H'_{\omega K + 2l + 2} &= -4[X_{II}(l+1) + (A-B)(K+1) - A\zeta(K+l+2)], \\ H'_{\omega K l} - H'_{\omega K - 2l - 2} &= 4[X_{II}(l-1) + (A-B)(K-1) - A\zeta(K+l-2)], \\ H'_{\omega K l} - H'_{\omega K + 2l - 4} &= 8X_{II}(l-2) - 4(A-B)(K+1) - 4A\zeta(2K-l+4), \\ H'_{\omega K l} - H'_{\omega K - 2l + 4} &= -8X_{II}(l+2) + 4(A-B)(K-1) + 4A\zeta(2K-l-4). \end{aligned} \quad (A4)$$

from Bauer *et al.*<sup>14</sup> The Casimir functions were obtained from Townes and Schawlow.<sup>16</sup>

The first order energy correction of perturbation is

$$E^{(1)} = (v, J, K, l | H' | v, J, K, l)$$

and the second order energy is

$$\begin{aligned} E^{(2)} &= \sum_{i \neq j} \frac{H'_{ij}H'_{ji}}{E_i^{(0)} - E_j^{(0)}}, \\ \langle i | &= \langle v, J, K, l |, \\ | j \rangle &= | v, J, K \pm 2, l \pm 2 \rangle, | v, J, K \pm 1, l \mp 2 \rangle, \\ &\quad \times | v, J, K \pm 2, l \mp 4 \rangle. \end{aligned} \quad (A1)$$

From the diagonal matrix elements of the Hamiltonian

Finally, the rotational-vibrational energy for  $C_{3v}$  molecules is given by

$$E(v, J, K, l) = E_v + E^1 + E^2 + E_{\text{hfs}}. \quad (\text{A5})$$

By using the selection rule for the absorption spectrum

$$\Delta J = +1, \quad \Delta K = 0, \quad \Delta V = 0, \quad \Delta l = 0$$

we can get the frequency

$$\nu(v, J, K, l) = \frac{E(v, J+1, K, l) - E(v, J, K, l)}{h} + \Delta\nu(\text{hfs}). \quad (\text{A6})$$

Hence, the rotation frequency becomes

$$\nu(J, K, l) = A_1 + A_2 + A_3 + A_4 + A_5, \quad (\text{A7})$$

where

$$\begin{aligned} A_1 &\equiv \left\{ \begin{aligned} &2B_v(J+1) + 2\gamma_{ll}l^2(J+1) - 4D_v^J(J+1)^3 - 2D_{JK}^vK^2(J+1) \\ &+ 2N_v^Kl(J+1) + 4N_{JJ}^vKl(J+1)^3 + 2N_{JK}^vK^3l(J+1) \\ &+ H_J(J+1)^3[(J+2)^3 - J^3] + 4H_{JK}K^2(J+1)^3 + 2H_{JJK}K^4(J+1) \end{aligned} \right\}, \\ A_2 &\equiv \left\{ \frac{(v-l)(v+l+2)(J+1)[(J+1)^2 - (K+1)^2]q_v^2}{x_{ll}(l+1) + (A-B)(K+1) - A\zeta(K+l+2)} + \frac{(v+l)(v-l+2)(J+1)[(J+1)^2(K-1)^2]q_v^2}{x_{ll}(l-1) + (A-B)(K-1) - A\zeta(K+l-2)} \right\}, \\ A_3 &\equiv \left\{ \frac{2(v+l)(v-l+2)(J+1)[q_{12}(2K+1) + d_{12}(l-1)]^2}{4X_{ll}(l-1) - (A-B)(2K+1) - 2A\zeta(2K-l+2)} \right. \\ &\quad \left. - \frac{2(v-l)(v+l+2)(J+1)[q_{12}(2K-1) + d_{12}(l+1)]^2}{4X_{ll}(l+1) - (A-B)(2K-1) + 2A\zeta(-2K+l+2)} \right\}, \\ A_4 &\equiv \left\{ \left[ \frac{f_{24}^2(v-l)(v+l+2)(v+l+4)(v-l-2)}{8X_{ll}(l+2) - 4(A-B)(K-1) - 4A\zeta(2K-l-4)} \right] C_1^- \right. \\ &\quad \left. + \left[ \frac{f_{24}^2(v+l)(v-l+2)(v-l+4)(v+l-2)}{8X_{ll}(l-2) - 4(A-B)(K+1) - 4A\zeta(2K-l+4)} \right] C_1^+ \right\}, \end{aligned}$$

where

$$\begin{aligned} &[(J+1)(J+2) - K(K \mp 1)][(J+1)(J+2) - (K \mp 1)(K \mp 2)] \\ &- [J(J+1) - K(K \mp 1)][J(J+1) - (K \mp 1)(K \mp 2)] \equiv C_1^\mp, \\ A_5 &\equiv \left\{ eqQ \left[ \frac{3K^2}{J(J+1)} - 1 \right] \left[ \frac{3/4C(C+1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)} \right] + \nu(J, K, F) \right\}, \end{aligned}$$

where  $F = J-1, J, J+1$ ;  $C = F(F+1) - I(I+1) - J(J+1)$ ; and the spin-rotation term in the energy equation is

$$E_{\text{sr}}(J, K, F) = -C/2 \left[ C_N + \frac{(C_K - C_N)K^2}{J(J+1)} \right].$$

The term  $A_5$  contains both the spin-rotation and quadrupole interaction terms as expressed by Boucher *et al.*<sup>15</sup>

The terms  $A_2$  and  $A_4$  have accidental degeneracies in cases for  $Kl = 1$  and  $Kl = -2$ , respectively. In these cases these terms are replaced by energies obtained by direct diagonalization of the secular equation.

The final form of the frequency equation can be written as follows:

$$\begin{aligned} \nu(J, K, l) &= 2(J+1)[B_v + \gamma_{ll}l^2 - D_{JK}K^2 + \eta_{JK}Kl + \eta_{JK}K^3l] + \Delta\nu(\text{hfs}) - 4D_J(J+1)^3 + 4\eta_{JJ}Kl(J+1)^3 \\ &\quad - \left[ \frac{(v-l)(v+l+2)(J+1)[(J+1)^2 - (K+1)^2]q_v^2}{X_{ll}(l+1) + (A-B)_v(K+1) - A\zeta_v(K+l+2)} \right] + \left[ \frac{(v+l)(v-l+2)(J+1)[(J+1)^2 - (K-1)^2]q_v^2}{X_{ll}(l-1) + (A-B)_v(K-1) - A\zeta_v(K+l-2)} \right] \\ &\quad \left[ \begin{aligned} &\text{if } K = -1, l = -1 \text{ then } -2q_0(J+1)(v+1) \\ &\text{if } K = 1, l = 1 \text{ then } +2q_0(J+1)(v+1) \end{aligned} \right] \\ &\quad + \frac{2(v+l)(v-l+2)(J+1)[q_{12}(2K+1) + d_{12}(l-1)]^2}{4X_{ll}(l-1) - (A-B)_v(2K+1) - 2A\zeta_v(2K-l+2)} - \frac{2(v-l)(v+l+2)(J+1)[q_{12}(2K-1) + d_{12}(l+1)]^2}{4X_{ll}(l+1) - (A-B)_v(2K-1) + 2A\zeta_v(-2K+l+2)} \\ &\quad - \left[ \frac{f_{24}^2(v-l)(v+l+2)(v+l+4)(v-l-2)[(J+1)(J+2) - K(K-1)][(J+1)(J+2) - (K-1)(K-2)] - [J(J+1) - K(K-1)][J(J+1) - (K-1)(K-2)]}{8X_{ll}(l+2) - 4(A-B)_v(K-1) - 4A\zeta_v(2K-l-4)} \right] \\ &\quad \left[ \begin{aligned} &\text{if } l = -2, K = 1 \text{ then } -2f_{24}v(v+2)(J+1) \\ &\text{if } l = 2, K = -1 \text{ then } +2f_{24}v(v+2)(J+1) \end{aligned} \right] \\ &\quad + \left[ \frac{f_{24}^2(v+l)(v-l+2)(v-l+4)(v+l-2)[(J+1)(J+2) - K(K+1)][(J+1)(J+2) - (K+1)(K+2)] - [J(J+1) - K(K+1)][J(J+1) - (K+1)(K+2)]}{8X_{ll}(l-2) - 4(A-B)_v(K+1) - 4A\zeta_v(2K-l+4)} \right] \quad (\text{A8}) \end{aligned}$$

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