Comments on Quartic Centrifugal Distortion Constants for Asymmetric Top Molecules[1]

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Explicit relations between the spectroscopic constants, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K, obtained by the application of the various reduction procedures of the effective rotational Hamiltonian are given in matrix formulation. Watson's reduction procedures for the three different axis representations $\mathrm{I^r}$, $\mathrm{II^r}$, and $\mathrm{III^r}$ have been considered as well as the reduction making $\tilde{R}_5=0$, instead of $\tilde{R}_6=0$.

The ambiguity in the determination of the τ's arising from the use of planarity conditions is discussed in relation to the τ defect.

I. Introduction

Since the treatment of centrifugal distortion in the rotational spectra of molecules was considered rigorously by Watson[1–3], many molecules have been analyzed using Watson's reduced Hamiltonian. The centrifugal distortion constants thus obtained give information about the molecular force field and in some cases about the vibration-rotation interactions. The purpose of the present paper is to clarify several problems which arise in using reported centrifugal distortion constants.

To compare rotational and centrifugal distortion constants obtained for different molecules we have to use constants which are defined uniquely. Watson's determinable parameters are appropriate for the purpose, because they do not depend on any unitary transformation of the effective rotational Hamiltonian. On the other hand the spectroscopic constants, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K, are dependent on a unitary transformation and especially on the choice of the axis system. Although these constants are directly related to the form of the molecular spectra and are commonly reported, they can not be used for comparison with those obtained by some different reduction of the rotational Hamiltonian. Thus explicit relations between the spectroscopic constants for the various reduction procedures are desired.

In Sect. II of this paper, the relations among the spectroscopic constants in Watson's reduced Hamiltonian,

$$\begin{aligned}\tilde{\mathcal{H}} = {} & \tfrac{1}{2}(\tilde{X}+\tilde{Y})\hat{J}^2 + \{\tilde{Z}-\tfrac{1}{2}(\tilde{X}+\tilde{Y})\}\hat{J}_z^{\,2} \\ & -\Delta_J\hat{J}^4 - \Delta_{JK}\hat{J}^2\hat{J}_z^{\,2} - \Delta_K\hat{J}_z^{\,4} \\ & + (\hat{J}_x^{\,2}-\hat{J}_y^{\,2})\{\tfrac{1}{4}(\tilde{X}-\tilde{Y}) - \delta_J\hat{J}^2 - \delta_K\hat{J}_z^{\,2}\} \\ & + \{\tfrac{1}{4}(\tilde{X}-\tilde{Y}) - \delta_J\hat{J}^2 - \delta_K\hat{J}_z^{\,2}\}(\hat{J}_x^{\,2}-\hat{J}_y^{\,2}) + \dots,\end{aligned} \tag{1}$$

for the axis representations $\mathrm{I^r}$, $\mathrm{II^r}$, and $\mathrm{III^r}$, are discussed. The operators for the total angular momentum and its components are given in the above Hamiltonian by $\hat{J}$, $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$, respectively. The constants $\tilde{X}$, $\tilde{Y}$, and $\tilde{Z}$ are Watson's reduced rotational constants.

The Hamiltonian expressed by Eq. (1) is obtained by operating on Kivelson and Wilson's[4] rotational Hamiltonian,

$$\mathcal{H} = X\hat{J}_x^{\,2} + Y\hat{J}_y^{\,2} + Z\hat{J}_z^{\,2} + \tfrac{1}{4}\sum_{\alpha,\beta}\tau'_{\alpha\alpha\beta\beta}\hat{J}_\alpha^{\,2}\hat{J}_\beta^{\,2}\,, \tag{2}$$

with the unitary transformation $\hat{U}$, which is given by

$$\hat{U} = \exp\,[i\,s_{111}(\hat{J}_x\hat{J}_y\hat{J}_z + \hat{J}_z\hat{J}_y\hat{J}_x)]\,, \tag{3}$$

where

$$s_{111} = -4\,R_6/(X-Y)\,. \tag{4}$$

We thus obtain

$$\tilde{\mathcal{H}} = \hat{U}^{-1}\mathcal{H}\,\hat{U}\,. \tag{5}$$

The constants X, Y, Z, in Eqs. (2) and (4) are the unreduced effective rotational constants. They are equivalent to Kivelson and Wilson's β, γ, α, respectively. The constant R_6 in Eq. (4) is one of Nielsen's centrifugal distortion constants[5].

In order to reduce the number of parameters from nine (three rotational constants and six quartic centrifugal distortion constants) to eight which is the number of determinable parameters up to quartic terms, we can use any unitary transforma-

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tion which makes one linear combination of those nine parameters vanish. By the unitary transformation given by Eqs. (3) and (4), we can eliminate the terms with R_6 from the Hamiltonian and the $\Delta K = \pm 4$ matrix elements of the Hamiltonian vanish using the basis of symmetric-top wavefunctions.

Another useful unitary transformation reducing the Hamiltonian is that in which the terms with R_5, another one of Nielsen's constants, are eliminated, proposed by Winnewisser[6] and van Eijck[7]. This reduction procedure can be important in some special cases. In Sect. III of this paper the relation between the spectroscopic constants obtained by the $\tilde{R}_6 = 0$ reduction and by the $\tilde{R}_5 = 0$ reduction is discussed.

In the last Sect. (IV) the use of the planarity conditions for the centrifugal distortion constants is discussed. As pointed out by several authors[8–11], in a planar molecule, the non-vanishing, centrifugal distortion constants, τ_{aabb}, τ_{bbcc}, τ_{ccaa}, τ_{abab}, can not be determined uniquely from the five determinable centrifugal distortion constants and the planarity relations. They depend on the way of selecting the planarity relations. The differences between those obtained by the different selections are linearly dependent on the τ defect, which gives an indication of the limit of validity of the planarity relations.

The following notation is used in this paper:

$$T_{\alpha\alpha} = \tau'_{\alpha\alpha\alpha\alpha}/4 = \hbar^4 \tau_{\alpha\alpha\alpha\alpha}/4 \ (\alpha = x, y, z \text{ or } a, b, c)\,,$$
$$T_1 = \tau_1/4 = (\tau'_{xxyy} + \tau'_{yyzz} + \tau'_{zzxx})/4\,,$$
$$T_2 = \tau_2/4 = (X\tau'_{yyzz} + Y\tau'_{zzxx} + Z\tau'_{xxyy})/4\,,$$
$$T_{\alpha\beta} = \hbar^4 \tau_{\alpha\alpha\beta\beta}/4 \ (\alpha, \beta = x, y, z \text{ or } a, b, c)\,,$$
$$T^*_{ab} = \hbar^4 \tau_{abab}/4\,.$$

The remaining notation is the same as that used by Watson[1–3].

II. Dependence on the Axis Representation

By the unitary transformation of the effective rotational Hamiltonian which reduces the $\tilde{R}_6$ constant to zero, we get five reduced quartic centrifugal distortion constants, Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K. Watson's determinable parameters are related to those spectroscopic constants by

$$\boldsymbol{T} = \mathsf{Q}\,\boldsymbol{D} \tag{6}$$

where $\boldsymbol{T}$ is a column vector of the determinable centrifugal distortion constants and $\boldsymbol{D}$ is a column vector of the spectroscopic, or reduced, constants:

$$\boldsymbol{T} = \begin{bmatrix} T_{xx} \\ T_{yy} \\ T_{zz} \\ T_1 \\ T_2 \end{bmatrix} \quad \text{and} \quad \boldsymbol{D} = \begin{bmatrix} \Delta_J \\ \Delta_{JK} \\ \Delta_K \\ \delta_J \\ \delta_K \end{bmatrix}. \tag{7}$$

The transformation matrix in Eq. (6) is given by Eqs. (24), (31) of Ref.[3]:

$$\mathsf{Q} = \begin{bmatrix} -1 & 0 & 0 & -2 & 0 \\ -1 & 0 & 0 & 2 & 0 \\ -1 & -1 & -1 & 0 & 0 \\ -3 & -1 & 0 & 0 & 0 \\ -(X+Y+Z) & -(X+Y)/2 & 0 & X-Y & X-Y \end{bmatrix}, \tag{8}$$

where X, Y, and Z are the unreduced effective rotational constants.

The vector $\boldsymbol{T}$ depends on the axis representation and is not convenient to use. We define the vector $\boldsymbol{T}_0$ as

$$\boldsymbol{T}_0 = \begin{bmatrix} T_{aa} \\ T_{bb} \\ T_{cc} \\ T_1 \\ T_2 \end{bmatrix}. \tag{9}$$

The vector $\boldsymbol{T}_0$ is invariant under any cyclic permutation of the molecule-fixed axis representation, and invariant under any unitary transformation of the type of Equation (3). The matrix and the vector corresponding to Q and $\boldsymbol{D}$, however, depend on the choice of the axis representation. For the $\mathrm{I^r}$, $\mathrm{II^r}$, and $\mathrm{III^r}$ axis representations[12], Eq. (6) is rewritten as follows:

$$\boldsymbol{T}_0 = \mathsf{Q}_i \boldsymbol{D}_i\,, \quad (i = \mathrm{I, II, and\ III}) \tag{10}$$

where the subscripts represent the axis system. The right hand coordinate systems only are considered in the present work. Thus the superscript r is omitted in indicating the axis representation in the following equations. Comparing Eqs. (6) and (10) the matrix Q for the $\mathrm{I^r}$ axis representation is obtained from Eq. (8) as

$$\mathsf{Q}_{\mathrm{I}} = \begin{bmatrix} -1 & -1 & -1 & 0 & 0 \\ -1 & 0 & 0 & -2 & 0 \\ -1 & 0 & 0 & 2 & 0 \\ -3 & -1 & 0 & 0 & 0 \\ -(A+B+C) & -(B+C)/2 & 0 & B-C & B-C \end{bmatrix}. \tag{11}$$

	I^r	II^r	III^r
X	B	C	A
Y	C	A	B
Z	A	B	C

Table I. Choice of axis representation.

The identification of A, B, C with X, Y, Z is given in Table I. The other two matricies, Q_{II} and $\mathsf{Q}_{\mathrm{III}}$, are obtained by cyclic permutation of the first three rows and of A, B, and C in the last row of the matrix Q_{I} (see Appendix).

The inverse transformation of Eq. (6) is

$$\boldsymbol{D} = \mathsf{Q}^{-1} \boldsymbol{T}, \tag{12}$$

where Q^{-1}, the inverse matrix of Q, is given by Eqs. (51), (52) of Ref.[1]:

$$\mathsf{Q}^{-1} = \begin{bmatrix} -\frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 \\ \frac{3}{2} & \frac{3}{2} & 0 & -1 & 0 \\ -1 & -1 & -1 & 1 & 0 \\ -\frac{1}{4} & \frac{1}{4} & 0 & 0 & 0 \\ \dfrac{X-Z}{2(X-Y)} & \dfrac{Y-Z}{2(X-Y)} & 0 & -\dfrac{X+Y}{2(X-Y)} & \dfrac{1}{X-Y} \end{bmatrix}. \tag{13}$$

The inverse transformation of Eq. (10) is written as

$$\boldsymbol{D}_i = \mathsf{Q}_i^{-1} \boldsymbol{T}_0, \quad (i = \mathrm{I, II, and\ III}). \tag{14}$$

The matrix Q_i^{-1}, the inverse matrix of Q_i, can be obtained from Q^{-1} in Eq. (13) by the identification of A, B, C with X, Y, Z and by the appropriate permutations of the columns for a given axis representation: for example, in the I^r axis representation,

$$\mathsf{Q}_{\mathrm{I}}^{-1} = \begin{bmatrix} 0 & -\frac{1}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & \frac{3}{2} & \frac{3}{2} & -1 & 0 \\ -1 & -1 & -1 & 1 & 0 \\ 0 & -\frac{1}{4} & \frac{1}{4} & 0 & 0 \\ 0 & \dfrac{B-A}{2(B-C)} & \dfrac{C-A}{2(B-C)} & -\dfrac{B+C}{2(B-C)} & \dfrac{1}{B-C} \end{bmatrix}. \tag{15}$$

The inverse matricies of Q_{II} and $\mathsf{Q}_{\mathrm{III}}$, that is $\mathsf{Q}_{\mathrm{II}}^{-1}$ and $\mathsf{Q}_{\mathrm{III}}^{-1}$, are obtained by cyclic permutation of the first three columns and of A, B, and C in the last row of the matrix $\mathsf{Q}_{\mathrm{I}}^{-1}$ (see Appendix).

The relations between the reduced centrifugal distortion constants defined for the different axis representations are thus given as

$$\boldsymbol{D}_j = \mathsf{Q}_j^{-1} \mathsf{Q}_i \boldsymbol{D}_i, \quad (i, j = \mathrm{I, II, and\ III}). \tag{16}$$

For example, the product matrix which transforms the constants in the I^r representation into those in the III^r representation (see Appendix for others) is

$$\mathsf{Q}_{\mathrm{III}}^{-1} \mathsf{Q}_{\mathrm{I}} = \begin{bmatrix} 1 & \frac{1}{2} & \frac{1}{2} & 1 & 0 \\ 0 & -\frac{1}{2} & -\frac{3}{2} & -3 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & \frac{1}{4} & \frac{1}{4} & -\frac{1}{2} & 0 \\ 0 & 0 & -\dfrac{A-C}{2(A-B)} & 0 & \dfrac{B-C}{A-B} \end{bmatrix}. \tag{17}$$

The reduced rotational constants $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ are also dependent on the axis representation. These can be obtained from the expression of the determinable rotational constants $\mathfrak{A}$, $\mathfrak{B}$, and $\mathfrak{C}$, using the transformation relations of the centrifugal distortion constants described above. The Eqs. (54) in Ref.[1] are expressed in vector form as

$$\begin{bmatrix} \tilde{X} \\ \tilde{Y} \\ \tilde{Z} \end{bmatrix} = \begin{bmatrix} \mathfrak{X} \\ \mathfrak{Y} \\ \mathfrak{Z} \end{bmatrix} + \mathsf{C} \boldsymbol{D}, \tag{18}$$

where

$$\mathsf{C} = \begin{bmatrix} -2 & -1 & 0 & 2 & 2 \\ -2 & -1 & 0 & -2 & -2 \\ -2 & 0 & 0 & 0 & 0 \end{bmatrix}. \tag{19}$$

This equation is rewritten as

$$\begin{bmatrix} \tilde{A}_i \\ \tilde{B}_i \\ \tilde{C}_i \end{bmatrix} = \begin{bmatrix} \mathfrak{A} \\ \mathfrak{B} \\ \mathfrak{C} \end{bmatrix} + \mathsf{C}_i \boldsymbol{D}_i \tag{20}$$

where $i = \mathrm{I}$, II, and III, which indicates the axis representation. The axis dependent matrix C_i is obtained by the appropriate cyclic permutation of rows in the matrix C. Thus the differences between the reduced rotational constants in two different axis representations are given by

$$\begin{bmatrix} \tilde{A}_i - \tilde{A}_j \\ \tilde{B}_i - \tilde{B}_j \\ \tilde{C}_i - \tilde{C}_j \end{bmatrix} = \mathsf{C}_i \boldsymbol{D}_i - \mathsf{C}_j \boldsymbol{D}_j = (\mathsf{C}_i \mathsf{Q}_i^{-1} \mathsf{Q}_j - \mathsf{C}_j) \boldsymbol{D}_j. \tag{21}$$

Carpenter[13] reported the centrifugal distortion constants of F_2CO and SO_2 obtained by fitting the data separately to each of the three axis representations. In Table II these reported constants are compared with those obtained by the transformations derived here.

III. Use of the $\tilde{R}_5 = 0$ Reduction

If we use the unitary transformation, Eq. (3), with $s_{111} = 2 R_5 / (2Z - X - Y)$, we can reduce the constant $\tilde{R}_5$ to zero. Watson's choice, that is the

Table II. Centrifugal distortion constants in the various axis representations in MHz.

		I^r	II^r		III^r	
		Obs. [a]	Obs. [a]	Converted [b]	Obs. [a]	Converted [b]
SO_2	Δ_J	$6.5875(263)\times10^{-3}$	1.2418(6)	1.2412	1.2445(7)	1.2446
	Δ_{JK}	$-1.1724(36)\times10^{-1}$	$-3.8248(18)$	-3.8211	$-3.8326(23)$	-3.8313
	Δ_K	2.5899(10)	2.5934(13)	2.5899	2.5918(17)	2.5899
	δ_J	$1.7008(38)\times10^{-3}$	$-6.1898(27)\times10^{-1}$	-6.1902×10^{-1}	$6.1703(34)\times10^{-1}$	6.1731×10^{-1}
	δ_K	$2.5259(292)\times10^{-2}$	1.2559(6)	1.2564	$-1.3324(8)$	-1.3332
F_2CO	Δ_J	$6.1587(1155)\times10^{-3}$	$8.6508(1137)\times10^{-3}$	8.6520×10^{-3}	$1.3875(162)\times10^{-2}$	1.3904×10^{-2}
	Δ_{JK}	$-3.0051(2673)\times10^{-3}$	$-1.0475(297)\times10^{-2}$	-1.0485×10^{-2}	$-2.6140(254)\times10^{-2}$	-2.6242×10^{-2}
	Δ_K	$1.3244(213)\times10^{-2}$	$1.3233(214)\times10^{-2}$	1.3244×10^{-2}	$1.3207(263)\times10^{-2}$	1.3244×10^{-2}
	δ_J	$2.6261(380)\times10^{-3}$	$-3.8728(389)\times10^{-3}$	-3.8728×10^{-3}	$1.2589(380)\times10^{-3}$	1.2467×10^{-3}
	δ_K	$4.2959(1002)\times10^{-3}$	$-4.1805(990)\times10^{-3}$	-4.1847×10^{-3}	$-2.3471(390)\times10^{-1}$	-2.3247×10^{-1}

[a] Reported in Reference [13]. [b] Converted from the observed constants in the I^r axis representation.

$\tilde{R}_6=0$ reduction, has the advantage that the reduced Hamiltonian has no matrix elements for $\Delta K=\pm4$. Though the Hamiltonian obtained by the $\tilde{R}_5=0$ reduction loses this convenience for computation, the difficulty which appears with Watson's choice for very near symmetric-top molecules, for which the denominator in Eq. (4) is very small, can be avoided without changing the axis representation.

For the case $\tilde{R}_6=0$, the reduced rotational and centrifugal distortion constants are expressed in Eqs. (49), (50), (53) of Ref. [1]:

$$\begin{aligned}
&\tilde{X}=X-8(1+\sigma)R_6\,, \quad \tilde{Y}=Y-8(1-\sigma)R_6\,,\\
&\tilde{Z}=Z+16\,R_6\,, \quad \tilde{D}_J=D_J-2\,R_6=\Delta_J\,, \qquad (22)\\
&\tilde{D}_{JK}=D_{JK}+12\,R_6=\Delta_{JK}\,, \quad \tilde{D}_K=D_K-10\,R_6=\Delta_K\,,\\
&\tilde{\delta}_J=\delta_J\,, \quad \tilde{R}_5=R_5+2\,\sigma\,R_6=-\delta_K/2\,, \quad \tilde{R}_6=0\,,
\end{aligned}$$

where

$$\sigma=(2\,Z-X-Y)/(X-Y)\,.$$

On the other hand in the present choice, $\tilde{R}_5=0$, they are [7]

$$\begin{aligned}
&\tilde{X}'=X-4(b-1)R_5\,,\\
&\tilde{Y}'=Y-4(b+1)R_5\,,\\
&\tilde{Z}'=Z+8\,b\,R_5\,,\\
&\tilde{D}'_J=D_J-b\,R_5=\Delta'_J\,,\\
&\tilde{D}'_{JK}=D_{JK}+6\,b\,R_5=\Delta'_{JK}\,, \qquad (23)\\
&\tilde{D}'_K=D_K-5\,b\,R_5=\Delta'_K\,,\\
&\tilde{\delta}'_J=\delta_J=\delta'_J\,,\\
&\tilde{R}'_5=0\,, \quad \tilde{R}'_6=R_6-b\,R_5/2=-\delta'_K/2\,,
\end{aligned}$$

where

$$b=(Y-X)/(2\,Z-X-Y)=-1/\sigma\,.$$

The primes are used to distinguish between the constants for $\tilde{R}_6=0$ and for $\tilde{R}_5=0$. Comparing Eqs. (22) and (23) we obtain the following differences:

$$\begin{aligned}
\tilde{X}-\tilde{X}'&=-2(b-1)\,\delta_K=4(1+\sigma)\,\delta'_K\,,\\
\tilde{Y}-\tilde{Y}'&=-2(b+1)\,\delta_K=4(1-\sigma)\,\delta'_K\,,\\
\tilde{Z}-\tilde{Z}'&=4\,b\,\delta_K=-8\,\delta'_K\,, \qquad (24)
\end{aligned}$$

and

$$\begin{aligned}
\Delta_J-\Delta'_J&=-b\,\delta_K/2=\delta'_K\,,\\
\Delta_{JK}-\Delta'_{JK}&=3\,b\,\delta_K=-6\,\delta'_K\,,\\
\Delta_K-\Delta'_K&=-5\,b\,\delta_K/2=5\,\delta'_K\,, \qquad (25)\\
\delta_J-\delta'_J&=0\,,\\
\delta_K-\delta'_K&=(1+b/2)\,\delta_K=-(1-2\,\sigma)\,\delta'_K\,.
\end{aligned}$$

It is interesting to note that the right hand sides of the individual equations of Eqs. (24) and (25) are all parallel with each other. They give only one equation,

$$\delta_K=2\,\sigma\,\delta'_K\,. \qquad (26)$$

Now the transformation from the primed constants to Watson's constants may be expressed following Eq. (25) as

$$\boldsymbol{D}=\mathsf{P}\,\boldsymbol{D}'\,, \qquad (27)$$

where

$$\boldsymbol{D}'=\begin{bmatrix}\Delta'_J\\ \Delta'_{JK}\\ \Delta'_K\\ \delta'_J\\ \delta'_K\end{bmatrix} \qquad (28)$$

and

$$\mathsf{P}=\begin{bmatrix}1&0&0&0&1\\0&1&0&0&-6\\0&0&1&0&5\\0&0&0&1&0\\0&0&0&0&2\,\sigma\end{bmatrix}. \qquad (29)$$

The inverse transformation of this is

$$\boldsymbol{D}' = \mathsf{P}^{-1}\,\boldsymbol{D}\,, \tag{30}$$

where

$$\mathsf{P}^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 & b/2 \\ 0 & 1 & 0 & 0 & -3\,b \\ 0 & 0 & 1 & 0 & 5\,b/2 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & -b/2 \end{bmatrix}. \tag{31}$$

From Eqs. (6) and (27) the transformation from the primed constants to Watson's determinable constants is obtained:

$$\boldsymbol{T} = \mathsf{Q}'\,\boldsymbol{D}'\,, \tag{32}$$

where

$$\mathsf{Q}' = \mathsf{Q}\,\mathsf{P} \tag{33}$$

$$= \begin{bmatrix} -1 & 0 & 0 & -2 & -1 \\ -1 & 0 & 0 & 2 & -1 \\ -1 & -1 & -1 & 0 & 0 \\ -3 & -1 & 0 & 0 & 3 \\ -(X+Y+Z) & -(X+Y)/2 & 0 & X-Y & 3\,Z \end{bmatrix}.$$

The inverse transformation of this is

$$\boldsymbol{D}' = \mathsf{Q}'^{-1}\,\boldsymbol{T}\,, \tag{34}$$

where

$$\mathsf{Q}'^{-1} = \mathsf{P}^{-1}\,\mathsf{Q}^{-1} = \begin{pmatrix} -\dfrac{(3-b)}{8} & -\dfrac{(3+b)}{8} & 0 & \dfrac{(X+Y)}{4\,(2\,Z-X-Y)} & -\dfrac{1}{2\,(2\,Z-X-Y)} \\ \dfrac{3\,(1-b)}{4} & \dfrac{3\,(1+b)}{4} & 0 & -\dfrac{(4\,Z+X+Y)}{2\,(2\,Z-X-Y)} & \dfrac{3}{(2\,Z-X-Y)} \\ -\dfrac{(3-5\,b)}{8} & -\dfrac{(3+5\,b)}{8} & -1 & \dfrac{(8\,Z+X+Y)}{4\,(2\,Z-X-Y)} & -\dfrac{5}{2\,(2\,Z-X-Y)} \\ -\frac{1}{4} & \frac{1}{4} & 0 & 0 & 0 \\ -\dfrac{(1+b)}{8} & -\dfrac{(1-b)}{8} & 0 & -\dfrac{(X+Y)}{4\,(2\,Z-X-Y)} & \dfrac{1}{2\,(2\,Z-X-Y)} \end{pmatrix} \tag{35}$$

The dependence of the primed constants on the choice of the axis representation can be found in the same way as described in Section I.

For completeness, the direct relations between Watson's determinable rotational constants and the reduced primed constants are found by substituting Eq. (27) and Eq. (24) into Eq. (18):

$$\begin{bmatrix} \tilde{X}' \\ \tilde{Y}' \\ \tilde{Z}' \end{bmatrix} + 4\,\delta'_K \begin{bmatrix} 1+\sigma \\ 1-\sigma \\ -2 \end{bmatrix} = \begin{bmatrix} \mathfrak{X} \\ \mathfrak{Y} \\ \mathfrak{Z} \end{bmatrix} + \mathsf{C}\,\mathsf{P}\,\boldsymbol{D}'\,.$$

This equation is rewritten in a form similar to Eq. (18) as

$$\begin{bmatrix} \tilde{X}' \\ \tilde{Y}' \\ \tilde{Z}' \end{bmatrix} = \begin{bmatrix} \mathfrak{Y} \\ \mathfrak{X} \\ \mathfrak{Z} \end{bmatrix} + \mathsf{C}'\,\boldsymbol{D}' \tag{36}$$

where

$$\mathsf{C}' = \begin{bmatrix} -2 & -1 & 0 & 2 & 0 \\ -2 & -1 & 0 & -2 & 0 \\ -2 & 0 & 0 & 0 & 6 \end{bmatrix}. \tag{37}$$

IV. Use of the Planarity Conditions

There are seven centrifugal distortion constants for a planar molecule:

$$T_{aa}\,,\ T_{bb}\,,\ T_{cc}\,,\ T_{ab}\,,\ T_{bc}\,,\ T_{ca} \text{ and } T^{*}_{ab}\,.$$

However, only five constants can be determined from the analysis of a molecular spectrum:

$$T_{aa}\,,\ T_{bb}\,,\ T_{cc}\,,\ T_1 \text{ and } T_2\,.$$

The constants T_1 and T_2 are linear combinations of the last four constants of the former set:

$$T_1 = T_{ab} + T_{bc} + T_{ca} + 2\,T^{*}_{ab}\,, \tag{38}$$

$$T_2 = A\,T_{bc} + B\,T_{ca} + C\,T_{ab} + 2\,C\,T^{*}_{ab}\,. \tag{39}$$

In order to obtain the seven constants we have to use the planarity conditions:

$$T_{ab} = A^2\,B^2(-T_{aa}/A^4 - T_{bb}/B^4 + T_{cc}/C^4)/2\,, \tag{40}$$

$$T_{bc} = B^2\,C^2(-T_{aa}/A^4 + T_{bb}/B^4 + T_{cc}/C^4)/2\,, \tag{41}$$

$$T_{ca} = C^2\,A^2\,(T_{aa}/A^4 - T_{bb}/B^4 + T_{cc}/C^4)/2\,. \tag{42}$$

The above three equations are valid only when all the constants have the values corresponding to the equilibrium configuration of the molecule. It has been assumed, however, by many investigators that these equations hold also for the ground vibrational state constants within the range of experimental uncertainties given for the centrifugal distortion constants. Following this assumption we define here the constants in Eqs. (38) – (42) as follows: The constants A, B, C, T_{aa}, T_{bb}, T_{cc}, T_1 and T_2 are Watson's determinable parameters in the ground vibrational state, which are known constants.

Now we have five equations, Eqs. (38) – (42), relating four unknowns. This results in an ambiguity in the determination of the unknowns: from which four relations are the constants determined in a given case, and is there a preferred set of four relations which should be used? This problem was pointed out by Kirchhoff[8] and by Cook et al.[9, 10]. However, no detailed consideration has been made of this problem.

To clarify the relation between the above three planarity conditions and Watson's planarity condition,

$$\Delta T_{cc} = T_{cc} - (T_2 - C\,T_1)/(A+B) = 0\,, \qquad (43)$$

Eqs. (40) – (42) are rewritten as

$$T_{ca} = T_{aa}(C/A)^2 + T_{ab}(C/B)^2\,, \qquad (44)$$

$$T_{cc} = T_{ca}(C/A)^2 + T_{bc}(C/B)^2\,, \qquad (45)$$

$$T_{bc} = T_{ab}(C/A)^2 + T_{bb}(C/B)^2\,. \qquad (46)$$

Watson's condition, Eq. (43), may be shown to be equivalent to Equation (45). From Eqs. (38), (39), (43) and using the approximate relation

$$1/C = 1/A + 1/B \qquad (47)$$

we obtain

$$T_{cc} - \Delta T_{cc} = T_{bc}(C/B)^2 + T_{ca}(C/A)^2\,. \qquad (48)$$

Putting $\Delta T_{cc} = 0$ in Eq. (48), Eq. (45) is obtained. As will be shown below, the difference between Eq. (48) with non-zero ΔT_{cc} and Eq. (45) represents the magnitude of the ambiguity in determining the constants. The quantity ΔT_{cc} is called the τ defect in this paper.

The following five choices of linearly independent equations may be used.

Case 1. T_{ab}, T_{bc}, and T_{ca} are determined by Eqs. (40) – (42), and T^*_{ab} is then determined from Equation (38).

Case 2. T_{ab}, T_{bc}, and T_{ca} are determined by Eqs. (40) – (42), and T^*_{ab} is then determined from Equation (39).

Case 3. T_{ab} and T_{bc} are determined by Eqs. (40), (41), T_{ca} is determined by Eq. (48), and T^*_{ab} is then obtained from Eq. (38) or Equation (39).

Case 4. T_{ab} and T_{ca} are determined by Eqs. (40), (42), T_{bc} is determined by Eq. (48), and T^*_{ab} is then obtained from Eq. (38) or Equation (39).

Case 5. T_{ab}, T_{bc}, and T_{ca} are determined by Eqs. (44), (46), (48), and T^*_{ab} is then obtained from Eq. (38) or Equation (39).

The use of Eq. (48) allows us to express the differences between the five resulting sets of $T_{\alpha\beta}$'s in terms of ΔT_{cc}.

For simplicity we define the following constants as *standard:* Observed T_{aa}, T_{bb}, T_{cc}, and T_1, and $T_2{}^0$ which is T_2 calculated from the relation $\Delta T_{cc} = 0$. That is

$$T_2{}^0 = (A+B)\,T_{cc} + C\,T_1\,. \qquad (49)$$

To distinguish this *standard* from the observed T_2, we use here the notation $T_2{}^0$ for the *standard.* Since one of the planarity relations has been used to fix the value $T_2{}^0$, we have to use the other two planarity relations to obtain the unknown constants. Therefore we can determine $T_{ab}{}^0$, $T_{bc}{}^0$, $T_{ca}{}^0$, and T^{*0}_{ab}, where the superscript means *standard,* uniquely in the approximation of Equation (47).

The four unknown T's obtained in Case 1 have to coincide with those *standard* results, because all of the three planarity relations are used and T_2 is not used in the calculation.

In Case 2, T_{ab}, T_{bc}, and T_{ca} are the same as the *standard* values:

$$\delta T_{ab} = \delta T_{bc} = \delta T_{ca} = 0$$

where

$$\delta T_{\alpha\beta} = T_{\alpha\beta} - T_{\alpha\beta}{}^0\,, \quad (\alpha, \beta = a, b, c)\,.$$

The difference from the *standard* is expressed in this way hereafter. Since T_2 observed is different from $T_2{}^0$ by $-(A+B)\,\Delta T_{cc}$, the constant T^*_{ab}, which is obtained from T_2 in this case, is different from $T^{*\,0}_{ab}$ by

$$\delta T^*_{ab} = T^*_{ab} - T^{*\,0}_{ab} = -\,[(A+B)/(2\,C)]\,\Delta T_{cc}\,. \quad (50)$$

In Case 3, we obtain:

$$\begin{aligned} &\delta T_{ab} = \delta T_{bc} = 0\,. \\ &\delta T_{ca} = -\,(A/C)^2\,\Delta T_{cc}\,, \qquad (51) \\ \text{and}\quad &\delta T^*_{ab} = (A/C)^2\,\Delta T_{cc}/2\,. \end{aligned}$$

Since Eq. (48) contains a linear combination of Eqs. (38) and (39), the same T^*_{ab} is obtained both from Eq. (38) and Eq. (39) in the approximation of Equation (47). This situation holds for the next two cases also.

In Case 4, we obtain

$$\begin{aligned} &\delta T_{ab} = \delta T_{ca} = 0\,, \\ &\delta T_{bc} = -\,(B/C)^2\,\Delta T_{cc}\,, \qquad (52) \\ \text{and}\quad &\delta T^*_{ab} = (B/C)^2\,\Delta T_{cc}/2\,. \end{aligned}$$

In Case 5, since the set of Eqs. (44), (46), (48) is equivalent to the set of Eqs. (40), (41), (42) if T_{cc} is replaced by $T_{cc} - \Delta T_{cc}$, we arrive at

$$\begin{aligned} &\delta T_{ab} = -\,(A\,B/C^2)^2\,\Delta T_{cc}/2\,, \\ &\delta T_{bc} = -\,(B/C)^2\,\Delta T_{cc}/2\,, \qquad (53) \\ &\delta T_{ca} = -\,(A/C)^2\,\Delta T_{cc}/2\,, \\ \text{and}\quad &\delta T^*_{ab} = (A^2 B^2 + B^2 C^2 + C^2 A^2)\,\Delta T_{cc}/(4\,C^4)\,. \end{aligned}$$

Table III. The ambiguity originating from the planarity relations used to determine the constant $\tau_{abab}\hbar^4 = 4\,T^*_{ab}$ in MHz.

$\tau_{abab}\hbar^4$	Case 1	Case 2	Case 3	Case 4	Case 5
CH_2CHNC					
Reported [a]	−0.06795	−0.06719	−0.07507	−0.06803	−0.07597
This work [b]	−0.06795	−0.06717	−0.07541	−0.06803	−0.07628
H_2O					
Reported [c]	−124.4	−85.1	−194.1	—	—
This work [b]	−124.0	−90.6	−190.1	−141.9	−246.9
SSO					
Reported [d]	−0.0307	−0.0303	−0.0324	—	—
This work [b]	−0.0306	−0.0305	−0.0321	−0.0307	−0.0323

[a] Ref. 11. [b] Obtained from the observed constant in case 1. [c] Ref. 10. [d] Ref. 9.

Using the relations derived here, the differences between the constants obtained for the different methods of calculation listed above are reproduced successfully for several molecules as listed in Table III. The slight discrepancies which are found between the previously reported and the present values have two origins. First, the $\delta T_{\alpha\beta}$ values depend on the definition of the rotational constants used in the calculations; for example, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, instead of $\mathfrak{A}$, $\mathfrak{B}$, $\mathfrak{C}$. Second, the $\delta T_{\alpha\beta}$ values depend on whether the approximate relation Eq. (47) is used or not, indeed we can change the $\delta T_{\alpha\beta}$ expressions given above into various forms by the use of Equation (47).

Another method has frequently been used for planar molecules to determine four independent τ's, which is different from any one of the above five cases: the observed rotational frequencies are fitted to the unreduced Hamiltonian with the constraint of three planarity relations. Similarly it is also possible to fit the frequencies to a modified Watson's Hamiltonian for which one of the independent constants has been eliminated by applying the constraint $\Delta T_{cc} = 0$. It should be noted, however, that these methods, applying the planarity relations prior to the fitting procedure, produce a certain model error, the magnitude of which can not be estimated by the statistical treatment of the data. It is indeed a further disadvantage of these methods that we lose information about ΔT_{cc}.

The τ defect ΔT_{cc}, represents not only the vibrational dependence of the centrifugal distortion constants but also that of the rotational constants, since the ground state rotational constants are used in the definition of ΔT_{cc} and in the planarity relations in this discussion. It indicates the limitation of the validity of the planarity condition Equation (45). However, we can not estimate the errors in the other two planarity relations. Therefore, the ambiguity discussed here is only a part of the total ambiguity. It can be concluded that we should be careful to specify the planarity conditions used in any determination of the τ constants, and that the τ defect gives some information, though incomplete information, about the errors of the constants obtained by using the planarity relations.

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Appendix

The matricies $\mathbf{Q}_i$, which appear in Eq. (10), are as follows:

$$\mathbf{Q}_{\mathrm{I}} = \begin{bmatrix} -1 & -1 & -1 & 0 & 0 \\ -1 & 0 & 0 & -2 & 0 \\ -1 & 0 & 0 & 2 & 0 \\ -3 & -1 & 0 & 0 & 0 \\ -(A+B+C) & -(B+C)/2 & 0 & B-C & B-C \end{bmatrix}, \tag{a 1}$$

$$\mathbf{Q}_{\mathrm{II}} = \begin{bmatrix} -1 & 0 & 0 & 2 & 0 \\ -1 & -1 & -1 & 0 & 0 \\ -1 & 0 & 0 & -2 & 0 \\ -3 & -1 & 0 & 0 & 0 \\ -(A+B+C) & -(C+A)/2 & 0 & C-A & C-A \end{bmatrix}, \tag{a 2}$$

and

$$\mathbf{Q}_{\mathrm{III}} = \begin{bmatrix} -1 & 0 & 0 & -2 & 0 \\ -1 & 0 & 0 & 2 & 0 \\ -1 & -1 & -1 & 0 & 0 \\ -3 & -1 & 0 & 0 & 0 \\ -(A+B+C) & -(A+B)/2 & 0 & A-B & A-B \end{bmatrix}. \tag{a 3}$$

The inverse matricies Q_i^{-1}, which appear in Eq. (14) are as follows:

$$\mathrm{Q}_{\mathrm{I}}^{-1}=\begin{bmatrix} 0 & -1/2 & -1/2 & 0 & 0 \\ 0 & 3/2 & 3/2 & -1 & 0 \\ -1 & -1 & -1 & 1 & 0 \\ 0 & -1/4 & 1/4 & 0 & 0 \\ 0 & -\dfrac{A-B}{2(B-C)} & -\dfrac{A-C}{2(B-C)} & -\dfrac{B+C}{2(B-C)} & \dfrac{1}{B-C} \end{bmatrix}, \tag{a 4}$$

$$\mathrm{Q}_{\mathrm{II}}^{-1}=\begin{bmatrix} -1/2 & 0 & -1/2 & 0 & 0 \\ 3/2 & 0 & 3/2 & -1 & 0 \\ -1 & -1 & -1 & 1 & 0 \\ 1/4 & 0 & -1/4 & 0 & 0 \\ -\dfrac{A-B}{2(A-C)} & 0 & \dfrac{B-C}{2(A-C)} & \dfrac{A+C}{2(A-C)} & -\dfrac{1}{A-C} \end{bmatrix}, \tag{a 5}$$

and

$$\mathrm{Q}_{\mathrm{III}}^{-1}=\begin{bmatrix} -1/2 & -1/2 & 0 & 0 & 0 \\ 3/2 & 3/2 & 0 & -1 & 0 \\ -1 & -1 & -1 & 1 & 0 \\ -1/4 & 1/4 & 0 & 0 & 0 \\ \dfrac{A-C}{2(A-B)} & \dfrac{B-C}{2(A-B)} & 0 & -\dfrac{A+B}{2(A-B)} & \dfrac{1}{A-B} \end{bmatrix}. \tag{a 6}$$

The products of the matricies, $\mathrm{Q}_i^{-1}\,\mathrm{Q}_j$, which appear in Eq. (16), are as follows:

$$\mathrm{Q}_{\mathrm{II}}^{-1}\,\mathrm{Q}_{\mathrm{I}}=\begin{bmatrix} 1 & 1/2 & 1/2 & -1 & 0 \\ 0 & -1/2 & -3/2 & 3 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & -1/4 & -1/4 & -1/2 & 0 \\ 0 & 0 & \dfrac{A-B}{2(A-C)} & 0 & -\dfrac{B-C}{A-C} \end{bmatrix}, \tag{a 7}$$

and

$$\mathrm{Q}_{\mathrm{III}}^{-1}\,\mathrm{Q}_{\mathrm{I}}=\begin{bmatrix} 1 & 1/2 & 1/2 & 1 & 0 \\ 0 & -1/2 & -3/2 & -3 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1/4 & 1/4 & -1/2 & 0 \\ 0 & 0 & -\dfrac{A-C}{2(A-B)} & 0 & \dfrac{B-C}{A-B} \end{bmatrix}. \tag{a 8}$$

The other four product matricies can be obtained by changing the last row of the matrix in Eq. (a 7) and Equation (a 8).

For $\mathrm{Q}_{\mathrm{III}}^{-1}\,\mathrm{Q}_{\mathrm{II}}$, the last row of the matrix in Eq. (a 7) should be replaced by

$$[0, 0, -(B-C)/\{2(A-B)\},\quad 0, -(A-C)/(A-B)]\,. \tag{a 9}$$

For $\mathrm{Q}_{\mathrm{I}}^{-1}\,\mathrm{Q}_{\mathrm{III}}$, the last row of the matrix in Eq. (a 7) should be replaced by

$$[0, 0, (A-C)/\{2(B-C)\},\quad 0, (A-B)/(B-C)]\,. \tag{a 10}$$

For $\mathrm{Q}_{\mathrm{I}}^{-1}\,\mathrm{Q}_{\mathrm{II}}$, the last row of the matrix in Eq. (a 8) should be replaced by

$$[0, 0, (A-B)/\{2(B-C)\},\quad 0, -(A-C)/(B-C)]\,. \tag{a 11}$$

For $\mathrm{Q}_{\mathrm{II}}^{-1}\,\mathrm{Q}_{\mathrm{III}}$, the last row of the matrix in Eq. (a 8) should be replaced by

$$[0, 0, -(B-C)/\{2(A-C)\},\quad 0, -(A-B)/(A-C)]\,. \tag{a 12}$$

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