Calculation of the Centrifugal Distortion Constants Using Dependent Internal Coordinates, Numerical Example Cyclopentene

M. PETZUCH *

Sektion Physik der Universität München, W. Germany, Lehrstuhl Prof. BRANDMÜLLER

(Z. Naturforsch. **24 a**, 637—642 [1969]; received 8 January 1969)

A formula is derived for the calculation of the centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$ in the case where the vibration problem is solved by using dependent internal symmetry coordinates. We have calculated the τ's and the D's with this new formula for a model of cyclopentene with a planar carbon ring (Point group C_{2v}).

The τ-values calculated are (in units $10^{85}\ \sec^2(\text{gcm}^2)^{-3}$):

$$\tau_{xxxx} = -5.27, \quad \tau_{xxyy} = 1.48, \quad \tau_{xxzz} = -0.96,$$
$$\tau_{yyyy} = -5.52, \quad \tau_{yyzz} = -1.22, \quad \tau_{zzzz} = -0.63,$$
$$\tau_{xyxy} = -2.85, \quad \tau_{yzyz} = -0.07, \quad \tau_{zxzx} = -0.07.$$

The D's calculated are (in units $10^{-8}\ \text{cm}^{-1}$):

$$D_J = 7.9, \quad D_K = 5.1, \quad D_{JK} = -12.1.$$

The values for D_J and for D_{JK} are within the accuracy of the published experimental values.

Thus, cyclopentene is the first ring molecule, the centrifugal distortion constants of which could be calculated.

The term centrifugal distortion of polyatomic molecules was formulated mathematically in 1936 by WILSON and HOWARD[1]. In 1953 KIVELSON and WILSON[2] discussed the importance of the centrifugal constants as an additional source of information for evaluation of force constants of mechanical molecular models. On the other hand measured values of the centrifugal distortion constants of ring molecules have been available for 15 years.

However, up to now there has been no calculation of the centrifugal distortion constants of ring molecules for a given set of force constants. Therefore it was not possible to compare theoretical with experimental values, which is the first step to arrive at an improvement of the force constants by iteration. Partly this may be caused by the considerable numerical effort, especially in calculating the derivatives of the centrifugal distortion constants with respect to the force constants. In addition, there was the following difficulty. Ring molecules are treated most conveniently using dependent internal coordinates. Unfortunately, there were no formulae available for direct numerical evaluation.

In this paper[3,4] the formula is derived for the calculation of the centrifugal distortion constants by means of dependent internal coordinates. As a numerical example we have used cyclopentene.

I. Definitions

One defines as centrifugal distortion constants both the so called τ's and the so called D's. The D's are linear combinations of the τ's with constant coefficients.

The three following D's are the most important ones, because they are experimentally accessible for the symmetric and for the nearly symmetric rotor:

$$\begin{aligned} D_J &= -(\hbar^4/32)\,(3\,\tau_{xxxx} + 3\,\tau_{yyyy} + \\ &\qquad + 2\,\tau_{xxyy} + 4\,\tau_{xyxy})\,, \\ D_K &= D_J - (\hbar^4/4)\,(\tau_{zzzz} - \tau_{zzxx} - \\ &\qquad - \tau_{yyzz} - 2\,\tau_{yzyz} - 2\,\tau_{zxzx})\,, \\ D_{JK} &= -D_J - D_K - (\hbar^4/4)\,\tau_{zzzz}\,. \end{aligned} \tag{1}$$

Here, energy units are used.

The $\tau_{\alpha\beta\gamma\delta}(\alpha, \beta, \gamma, \delta = x, y, \text{or } z)$ are

$$\tau_{\alpha\beta\gamma\delta} = -\tfrac{1}{2} \sum_{k=1}^{3N-6} a_k^{\alpha\beta}\, a_k^{\gamma\delta} / \lambda_k\, I^0_{\alpha\alpha}\, I^0_{\beta\beta}\, I^0_{\gamma\gamma}\, I^0_{\delta\delta}\,. \tag{2}$$

Here, $\lambda_k = 4\,\pi^2\,\nu_k^2$, where ν_k is the frequency of the k^{th} normal vibration (harmonic component). Fur-

---

* Present address 1288 Oak Grove Avenue, San Marino, California 91108, USA.

[1] E. B. WILSON, Jr., and J. B. HOWARD, J. Chem. Phys. **4**, 260 [1936].

[2] D. KIVELSON and E. B. WILSON, Jr., J. Chem. Phys. **21**, 1229 [1953].

[3] M. PETZUCH, Thesis, Universität München 1967.

[4] M. PETZUCH, 9th European Congress on Molecular Spectroscopy, Madrid, Sept. 1967.

ther, N is the number of atoms in the molecule, and I^0_{xx}, I^0_{yy}, I^0_{zz} are the principal moments of inertia of the molecule in equilibrium ($I^0_{xx} < I^0_{yy} < I^0_{zz}$).

In addition, we have

$$a_k^{\alpha\alpha} = 2 \sum_{i=1}^{N} m_i^{1/2} (\beta_i^0 \, l_{ik}^{(\beta)} + \gamma_i^0 \, l_{ik}^{(\gamma)}) \, ,$$
$$a_k^{\alpha\beta} = - \sum_{i=1}^{N} m_i^{1/2} (\alpha_i^0 \, l_{ik}^{(\beta)} + \beta_i^0 \, l_{ik}^{(\alpha)}) \, . \tag{3}$$

In Eq. (3) $\alpha \neq \beta \neq \gamma$, and m_i is the mass of the i^{th} atom. The subscript "0" means "equilibrium value". The $l_{ik}^{(\varepsilon)}$, with ε standing for α, β, γ, are defined by the following transformation

$$m_i^{1/2} \Delta\varepsilon_i = \sum_{k=1}^{3N-6} l_{ik}^{(\varepsilon)} Q_k \, , \quad i = 1, \dots, N \, . \tag{4}$$

The $\Delta\varepsilon_i$ are the cartesian displacement coordinates of the i^{th} atom, and Q_k is the k^{th} normal coordinate of the molecule.

Inserting Eqs. (2) and (3) in Eq. (1) yields expressions, which, for example, are given by NIELSEN[5]. However, in the definition of Nielsen the D's have the dimensions of wave numbers (length^{-1}).

Thus, the τ's of a molecule can be calculated, if one knows its structure (equilibrium dimensions), its fundamental vibrational frequencies ν_k and the normal coordinates Q_k ($k = 1, \dots, N$). For convenience one defines

$$t_{\alpha\beta\gamma\delta} = - 2 \, (I^0_{\alpha\alpha} \, I^0_{\beta\beta} \, I^0_{\gamma\gamma} \, I^0_{\delta\delta}) \, \tau_{\alpha\beta\gamma\delta} \, . \tag{5}$$

II. $\tau_{\alpha\beta\gamma\delta}$ for Dependent Internal Coordinates

We want to calculate the frequencies ν_k and the normal coordinates Q_k by the method of WILSON, DECIUS, and CROSS[6]. To do this, we formulate the molecular motion in terms of internal coordinates. For a ring molecule like cyclopentene it is of advantage to use dependent internal coordinates. With this choice of coordinates the τ's can only be calculated by Eq. (2). If there are no redundant coordinates, we can equally well use Eq. (11) of KIVELSON and WILSON[2].

Let $\boldsymbol{q}$ be the column vector of the mass-weighted Cartesian displacement coordinates, and $\boldsymbol{Q}$ the column vector of the normal coordinates. Then Eq. (4) reads: $\boldsymbol{q} = \boldsymbol{l}\,\boldsymbol{Q}$. The formula for $\boldsymbol{l}$ was derived by STREY[7] for dependent internal coordinates.

Let $\boldsymbol{R}$ be the column vector of the dependent internal coordinates, and $\boldsymbol{S}$ the column vector of the dependent internal symmetry coordinates. Then the matrices $\boldsymbol{D}$, $\boldsymbol{U}$, and $\boldsymbol{L}$ are defined by $\boldsymbol{R} = \boldsymbol{D}\,\boldsymbol{q}$, $\boldsymbol{S} = \boldsymbol{U}\boldsymbol{R}$ and $\boldsymbol{S} = \boldsymbol{L}\boldsymbol{Q}$. The matrix $\boldsymbol{L}$ is derived from $\boldsymbol{G}\boldsymbol{F}\boldsymbol{L} = \boldsymbol{L}\Lambda$. Here, $\boldsymbol{G}$ is the matrix of the kinematic coefficients and $\boldsymbol{F}$ that of the force constants for internal symmetry coordinates. Further, Λ is the diagonal matrix if the

$$\lambda_k \, (k = 1, \dots, 3N-6) \, .$$

Then we have

$$\boldsymbol{l} = \widetilde{\boldsymbol{D}}\,\widetilde{\boldsymbol{U}}\boldsymbol{F}\boldsymbol{L}\,\Lambda^{-1}. \tag{6}$$

We denote by $\widetilde{\boldsymbol{M}}$ the transpose of a matrix $\boldsymbol{M}$.

Equation (5) is now to be written in matrix notation. Let $I_{\alpha\beta}$ ($\alpha = \beta$ or $\alpha \neq \beta$) be the elements of the inertia tensor. If l_{ik} are the elements of $\boldsymbol{l}$, and q_i the elements of $\boldsymbol{q}$, then for fixed subscript $\alpha\beta$ the derivative $(\partial I_{\alpha\beta}/\partial q)_0$ represents a column vector, which contains only the equilibrium coordinates. Accordingly, Eq. (3) reads

$$a_k^{\alpha\beta} = \sum_{i=1}^{3N} \widetilde{\left(\frac{\partial I_{\alpha\beta}}{\partial q_i}\right)_0} l_{ik} \, , \quad k = 1, \dots, 3N-6 \, . \tag{3a}$$

Now we have

$$t_{\alpha\beta\gamma\delta} = \sum_{k=1}^{3N-6} \left(\frac{1}{\lambda_k}\right)^3 \widetilde{\left(\frac{\partial I_{\alpha\beta}}{\partial q}\right)_0} \widetilde{\boldsymbol{D}}\,\widetilde{\boldsymbol{U}}\boldsymbol{F}\boldsymbol{L}_k \widetilde{\left(\frac{\partial I_{\gamma\delta}}{\partial q}\right)_0} \widetilde{\boldsymbol{D}}\,\widetilde{\boldsymbol{U}}\boldsymbol{F}\boldsymbol{L}_k . \tag{7}$$

Here, $\boldsymbol{L}_k$ is the k^{th} column of $\boldsymbol{L}$, i.e. eigenvector of λ_k. Equations (5) and (7) yield $\tau_{\alpha\beta\gamma\delta}$ for dependent internal symmetry coordinates.

The derivative of the t's and the τ's with respect to the force constants f_r is obtained by differentiating Eq. (7) and inserting the $(\partial\lambda_k/\partial f_r)$'s and $(\partial \boldsymbol{L}_k/\partial f_r)$'s given by STREY[7] for dependent internal coordinates.

III. Calculation of the τ's and D's for Cyclopentene

We have used cyclopentene as a numerical example for the following reasons. Firstly there are recently measured values of the centrifugal distortion constants, which are different however, for the

---

[5] H. H. NIELSEN, Rev. Mod. Phys. **23**, 90 [1951].

[6] E. B. WILSON, Jr., J. C. DECIUS, and P. C. CROSS, Molecular Vibrations, McGraw-Hill Book Co., New York 1955.

[7] G. STREY, J. Mol. Spectry **17**, 265 [1965].

different authors[8, 9, 10]. Secondly, a molecular model calculation of the vibrational frequencies has been made for the molecule using dependent internal coordinates[11].

In our first computations we tried to repeat the model calculation of SVERDLOV and KRAINOV[11]. We refer to our first computation in the following, especially in the tables, as "computation (I)". To get meaningful results we had to correct some misprints in their paper. Furthermore, we had to extend the model calculation to get the centrifugal distortion constants. We have used slightly different values for dimensions and force constants and slightly different definitions of the coordinates. These modifications are given below in the notation of Ref. [11].

For the angle ∢CCH between the carbon ring and the methylen group (Ref. [11]: Φ_1, Φ_2) we have used 110.34⁰ instead of 111.35⁰. Without this modification there would have been a contradiction with the other data. The remaining distances and angles were the same as in Ref [11]. With these data we got for the principal moments of inertia (units: 10^{-38} gcm^2): $I_{xx} = 1.14$, $I_{yy} = 1.19$, $I_{zz} = 2.18$ (see Fig. 1). These figures differ from the experimental values[12, 13] by a maximum of 3%. If we included in our model a bending of the carbon ring, as proposed in Refs. [12] and [13], the differences between theoretical and measured values of the inertia moments were less. However, to avoid a complication in the computation of centrifugal distortion constants, for the following calculation we have worked with a planar carbon ring. The difference between the two nearly equal inertia moments of cyclopentene is 1% experimentally, 5% for the model. Therefore it is a good approximation to treat the model, and even more the real molecule, as a symmetric rotor.

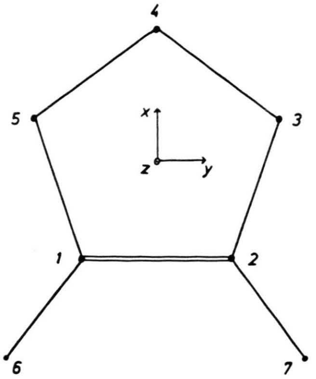

Fig. 1. Planar part of the cyclopentene molecule: Numbering of atoms and position of the coordinate system.

Only those internal coordinates which describe the motion of the carbon ring out of its plane are defined differently compared with Ref. [11]. Using the notation of Ref. [11] we define them as follows

$$\varrho_a^{b2} = -\frac{R}{a}\Delta z_1 + \frac{R\sin O_1}{r\sin(O_1+O_4)}(\Delta z_1 - \Delta z_6) + \frac{R\sin O_4}{b\sin(O_1+O_4)}(\Delta z_1 - \Delta z_5)\,,$$

$$\chi_c^{ab} = \frac{R\sin(O_1+O_2)}{b\sin O_1\sin O_2}(\Delta z_5 - \Delta z_1) + \frac{R}{a\sin O_1}(\Delta z_1 - \Delta z_2) + \frac{R}{c\sin O_2}(\Delta z_4 - \Delta z_5)\,,$$

$$\chi_{b2}^{e1} = \frac{R}{\sin(O_1+O_4)}\left\{\left(\frac{\cos O_4}{b} - \frac{\cos O_1}{r}\right)(\Delta z_1 - \Delta z_2) + \frac{\cos O_4}{b}(\Delta z_3 - \Delta z_5) + \frac{\cos O_1}{r}(\Delta z_6 - \Delta z_7)\right\}.$$

One obtains ϱ_a^{e1} form ϱ_a^{b2} by replacing in the subscript of Δz: 1 by 2, 6 by 7 and 5 by 3. Similarly one obtains χ_d^{ae} from χ_c^{ab}. Note, that all angle coordinates are multiplied by a fixed length ($R = 1.09$ Å) as is customary with Russian authors.

We obtained the redundancy conditions, two of which are not equal to those in Ref. [11]. Using the numbering of SVERDLOV and KRAINOV[11] we find $\gamma_{ab} + \gamma_{ae}$ instead of $\gamma_{ab} - \gamma_{ae}$ in their condition No. 7. Furthermore, we find $(\varrho_a^{b2} - \varrho_a^{e1})\cos O_1/\sin O_1$ instead of $(\varrho_b^{b2} - \varrho_a^{e1})\sin(O_1 + O_4)/(2\sin O_1\sin O_4)$ in their condition No. 9. This last correction seems to be attributable to our different definition of the coordinates.

The force constants belonging to these coordinates, however, have been used in this first calcul-

---

[8] B. J. MONOSTORI and A. WEBER, J. Mol. Spectry **15**, 158 [1965].

[9] S. I. SUBBOTIN, V. I. TYULIN, and V. M. TATEVSKII, Opt. and Spectry, **17**, 203 [1964].

[10] S. I. SUBBOTIN, V. I. TYULIN, C. I. KATAYEV, and V. M. TATEVSKII, Opt. and Spectry **19**, 361 [1965].

[11] L. M. SVERDLOV and E. N. KRAINOV, Opt. and Spectry **6**, 214 [1959]; Opt. i Spektroskopiya **6**, 334 [1959].

[12] G. W. RATHJENS, Jr., J. Chem. Phys. **36**, 2401 [1962].

[13] S. S. BUTCHER and C. C. COSTAIN, J. Mol. Spectry **15**, 40 [1965].

ation as in Ref. [11]. The numerical values of other force constants had to be chosen differently. For instance, we have taken $A_{ab}^{a} = 1$ (units: 10^6 cm^{-2})[14], extrapolating from the force constants of smaller molecules. The sign of $U_{c5}^{\chi_c}$ depends on the definition of the coordinates χ_c and β_{c5}; we have taken it positive.

We have assigned the symmetry coordinate $\chi_1^{A_2}$ or $\psi_1^{B_2}$ (see Ref. [11], p. 215) to the species B_2 or A_2, resp. instead of A_2 or B_2, respectively[11]. Only then can the matrix of the potential energy be reduced.

Like SVERDLOV and KRAINOV[11], we have used in our computations the "spectroscopic" mass of the hydrogen atom, which is 1.088 amu whereas the real mass is 1.008145 amu (C^{12}-scale). The values of the fundamental constants used in this paper are: Avogadro's number $N_a = 6.02252 \times 10^{23}$ mol^{-1}, velocity of light $c = 2.997925 \times 10^{10}$ cm/sec, Planck's constant $h = 6.6256 \times 10^{-27}$ erg sec.

The results of our slightly modified model calculation following Ref. [11], and of its extension to the calculation of the centrifugal distortion constants are given in Tables 3, 4 and 5 under "computation (I)".

In an improved second computation ("computation (II)") we started from the recently measured Raman- and infrared spectra of cyclopentene in the liquid phase, and used an assignment of the bands slightly different from Ref. [11]. In Table 1 are given the wave numbers and, in brackets, the corresponding depolarization ratios, referring to the integral intensity as obtained in our own measurements of the Raman spectrum in the liquid phase. As a first step we have assigned tentatively some lines in the following way:

2947 cm^{-1} in A_2, 2928 cm^{-1} in B_2, 2903 cm^{-1} in B_1, 1351 cm^{-1} in B_1, 1206 cm^{-1} in B_1, 1106 cm^{-1} in A_1, 770 cm^{-1} overtone, 625 cm^{-1} in B_2. Here, we have given the wave numbers according to our own measurements.

To get corrected force constants, we have checked which force constants affect mainly the newly assigned wave numbers, using the potential energy distribution according to our "computation (I)". Then, we have adjusted the wave numbers. The improved values of the modified or iterated force constants are given in Tab. 2 under "computation (II and III)". The remaining force constants used here are those of Ref. [11]. The changes in the numerical values of the force constants lead to reassignment of further vibrational bands. In Tab. 3 all reassigned lines are marked with a cross. The line at 770 cm^{-1} was assigned as an overtone. Our reassignment has the following advantages compared with the assignment of Ref. [11]: The strongly polarized line at 1106 cm^{-1} belongs to A_1. The narrow line at 1295 cm^{-1} is assigned to only one normal mode of vibration instead of five. The depolarization ratio of the lines of species A_1 in the new assignment is not greater than that of the lines of the other species. In this calculation we have used again the "spectroscopic" mass for hydrogen. The results of

3059 ± 2	(pol.)	1464 ± 2	(0.46 ± 0.10)	962 ± 2	(0.14 ± 0.05)
3052 ± 5		1439 ± 2	(0.74 ± 0.10)	936 ± 2	(dep.)
2947 ± 2		1351 ± 5		897 ± 2	(0.01 ± 0.05)
2928 ± 5		1295 ± 2	(0.20 ± 0.05)	811 ± 10	
2913 ± 5		1206 ± 2	(0.87 ± 0.05)	770 ± 5	(0.66 ± 0.15)
2903 ± 5		1106 ± 2	(0.52 ± 0.05)	698 ± 5	(0.74 ± 0.15)
2847 ± 2	(pol.)	1046 ± 5		625 ± 10	(0.75 ± 0.15)
1613 ± 2	(0.01 ± 0.05)	1024 ± 2	(0.86 ± 0.05)	605 ± 10	
				386 ± 2	(0.82 ± 0.05)

Table 1. Wave numbers of the Raman spectrum in liquid phase (units: cm^{-1}) and in brackets the depolarization ratio.

	A_{13}^{b}	a_{a1}^{1}	K_{a2}	n_{a1}^{a2}	m_{ab}^{a1}	K_{b2}	K_{ϱ}	$U_{\varrho 1}^{\varrho 2}$
Computation (I)	0.43	0.66	0.77	-0.025	0.095	0.7	0.317	0.047
Computation (II and III)	0.6	0.3	0.47	-0.13	0.06	0.76	0.273	0.0033

Table 2. Values of the modified or iterated force constants (units: 10^6 cm^{-2}).

---

[14] In the Russian papers, force constants are given in units of 10^6 cm^{-2}. To get them in units 10^5 dyn/cm we have to multiply the numerical value by 0.6365.

Coordinates	Symmetry	Computation (I)	Experimental[11]	Experimental	Computation (II)	Computation, harmonic frequencies (III)
$Q(\mathrm{C{=}C})$	A_1	1620	1614	1613	1616	1622
$Q(\mathrm{C{-}C})$	B_1	1114	1108	?/1130 x	1152	1159
$Q(\mathrm{C{-}C})$	A_1	962	965	962	966	979
$Q(\mathrm{C{-}C})$	B_1	904	937	936	919	932
$Q(\mathrm{C{-}C})$	A_1	903	900	897	905	913
$\gamma(\mathrm{CCC})$	B_1	706	702/692	698	691	692
$\gamma(\mathrm{CCC})$	A_1	628	603	605	613	616
$\beta(\mathrm{C{=}C{-}H})$	B_1	1419	?/1432	1351 x	1349	1384
$\beta(\mathrm{C{=}C{-}H})$	A_1	1211	1207/1213	1106 x	1102	1140
$\varrho_{\mathrm{CCH}}^{\mathrm{C=C}}$	A_2	982	1082	1024 ? x	981	1006
$\varrho_{\mathrm{CCH}}^{\mathrm{C=C}}$	B_2	771	772/762	625 x	645	668
$\chi_{\mathrm{CCH}}^{\mathrm{CCH}}$	A_2	414	387	387	414	422
$\chi_{\mathrm{C=C}}^{\mathrm{C-C}}$	B_2	253	?	?	253	259
$\alpha_{56}(\mathrm{HCH})$	A_1	1491	1468	1464	1473	1525
$\alpha(\mathrm{HCH})$	B_1	1471	1468	?/1432 x	1458	1511
$\alpha(\mathrm{HCH})$	A_1	1436	1441/1449	1439	1431	1482
$q(\mathrm{{=}C{-}H})$	A_1	3058	3060/3066	3059	3054	3162
$q(\mathrm{{=}C{-}H})$	B_1	3029	?	3052 x	3040	3148
$q^+(\mathrm{C{-}H})_{56}$	A_1	2847	2849	2847	2847	2951
$q^-(\mathrm{C{-}H})_{56}$	B_2	2894	2898	2928 x	2894	2995
$q^+(\mathrm{C{-}H})$	A_1	2909	2916	2913	2909	3015
$q^+(\mathrm{C{-}H})$	B_1	2907	?/2927	2903 x	2907	3014
$q^-(\mathrm{C{-}H})$	B_2	2958	?/2958	?/2958	2958	3062
$q^-(\mathrm{C{-}H})$	A_2	2957	?	2947 x	2957	3060
$\varphi_1(\mathrm{CCH})$	A_1	1334	1297/1356	1295	1271	1300
$\varphi_2(\mathrm{CCH})$	B_1	1318	1297	?/1281	1290	1325
$\varphi_1(\mathrm{CCH})$	B_1	1302	1297	1206 x	1216	1257
$\chi_1(\mathrm{CCH})$	B_2	1284	1297/1284	? x	1284	1325
$\chi_2(\mathrm{CCH})$	A_2	1288	1297	? x	1288	1335
$\chi_1(\mathrm{CCH})$	A_2	1184	1207	? x	1184	1224
$\psi_1(\mathrm{CCH})$	B_2	1070	1027/1048	?/1046	1065	1088
$\psi_1(\mathrm{CCH})$	A_2	833	800	811	833	859
$\psi_2(\mathrm{CCH})$	B_2	687	702	698	718	741

Table 3. Comparision of calculated with experimental wave numbers (units: cm^{-1}). Values following the stroke, e.g./1130, mean IR-lines. Wave numbers marked with a "x" are reassigned.

this calculation are given in Tab. 3 under "computation (II)".

The force constants derived in this procedure and the real hydrogen mass then yielded the "harmonic" vibrational frequencies, i.e. frequencies, into which no anharmonic contribution was introduced by the calculation. These results are given in Tab. 3 under "computation, harmonic frequencies (III)".

The detailed description of our calculations are given in Ref. [3]. The centrifugal distortion constants calculated are presented in Tabs. 4 and 5.

	D_J	D_K	D_{JK}
I)	7.81	4.98	− 11.80
II)	7.94	5.10	− 12.06
III)	7.73	5.02	− 11.80

Table 5. Calculated centrifugal distortion constants D_J, D_K, D_{JK} (units: 10^{-8} cm^{-1}). The D's are obtained from those defined in Eq. (1) by division through $h\,c$. (I, II, III as in Table 4.)

The results of our three calculations do not differ much in comparison with the relative errors of at

	τ_{xxxx}	τ_{xxyy}	τ_{xxzz}	τ_{yyyy}	τ_{yyzz}	τ_{zzzz}	τ_{xyxy}	τ_{yzyz}	τ_{zxzx}
I)	− 5.26	1.44	− 0.98	− 5.40	− 1.20	− 0.64	− 2.77	− 0.07	− 0.07
II)	− 5.27	1.48	− 0.96	− 5.52	− 1.22	− 0.63	− 2.85	− 0.07	− 0.07
III)	− 5.12	1.46	− 0.93	− 5.39	− 1.19	− 0.61	− 2.79	− 0.06	− 0.06

Table 4. Calculated centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$ (units: 10^{85} $\mathrm{sec}^2\,\mathrm{g}^{-3}\,\mathrm{cm}^{-6}$); compare Fig. 1 for the choice of the coordinate system. I = "Computation (I)", II = "Computation (II)", III = "Computation, harmonic frequencies (III)".

least 30% in the experimental data. The potential energy distribution of the D's (see Ref. [3]) indicates that the centrifugal distortion results from the carbon ring with its relatively heavy atoms.

The assignment of the fundamentals of the ring skeleton are the same in computations (I), and (II). Therefore it is reasonable that the results from calculations (I) and (II) do not differ very much.

The correction for anharmonicity concerns only the hydrogen atoms, which do not contribute appreciably to the centrifugal distortion constants. It is understandable, therefore, that the results of computation (III) do not differ much from those of (I) and (II).

Accordingly, one would not expect that a more accurate measurement of the vibrational frequencies would result in greatly improved centrifugal distortion constants. More of an improvement is to be expected from a reassignment of the vibrations of the ring skeleton by means of spectra of deuterated cyclopentene, or from a change of the geometrical model.

IV. Comparison of Calculated and Experimental *D*-Values of Cyclopentene

The numerical values of the centrifugal distortion constants τ, and of some quantities derived from them, determine whether the rotational diagonalization of the Hamilton operator is feasible[5]. Numerical inspection of the non-diagonal elements shows that this diagonalization indeed is feasible in the case of cyclopentene. Thus we have for cyclopentene, as for any symmetric rotor, an exact relation between the D's and the rotational energy. Therefore we can compare the calculated D-values with those evaluated for the S-branch of the measured rotation spectrum.

Measured D-values are given by MONOSTORI and WEBER[8] and by SUBBOTIN et al.[9,10] (see Table 6). MONOSTORI and WEBER[8] had a resolution three times that of SUBBOTIN et al.[9,10] and have recorded one spectrogram more. However, Ref. [8] reports a reproducibility of the measured lines "better than 0.03 cm^{-1}". Thus, as three spectrograms were recorded, the mean error of the wave number of a line can be still 0.01 to 0.02 cm^{-1}. Therefore it is questionable whether the fifth decimal of the given wave numbers is valid, and whether the accuracy of the D-values given by MONOSTORI and WEBER[8] can be verified by the measured data. On the other hand, SUBBOTIN et al. have given mean errors of such a magnitud that their D-values can only be considered as estimates. It seems to the author to be a matter of opinion, which of the two results is more reliable.

	Experimental[9,10]	Experimental[8]	Theoret.
D_J	$(3 \pm 5) \times 10^{-7}$	$(3.75 \pm 1.25) \times 10^{-8}$	7.9×10^{-8}
D_{JK}	$-(2 \pm 7) \times 10^{-6}$		-12.1×10^{-8}

Table 6. Comparision of calculated with experimental values of D_J and D_{JK} (units: cm^{-1}).

According to the data given in Table 6 the calculated values for D_J and D_{JK} are in reasonable agreement with the experimental values, if we keep in mind the reservation to be held with respect to the mean error given by Ref [8]. Thus the calculation seems to be well confirmed by the experimental data available.

Acknowledgements

I wish to thank Prof. J. BRANDMÜLLER for his interest in this work, and Dr. G. STREY for valuable discussions. The author was recipient of a predoctoral grant of the Stiftung Volkswagenwerk.