# Normal Coordinate Analysis and Mean Amplitudes of Vibration of Spiropentane

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Using spectroscopic data and structure parameters observed by electron diffraction, a normal coordinate analysis was performed for spiropentane. Harmonic force field, potential energy distribution and calculated mean amplitudes of vibration are reported. A very satisfactory agreement is found between observed and calculated mean amplitudes of vibration.

Recently a normal coordinate analysis of azulene was published [1]. The same paper also quotes several recently reported structural and spectral investigations on cyclic hydrocarbons. Many of the symmetry force constants arrived at there were well applicable as starting-point values for the corresponding force constants in the present investigation.

Dallinga et al. [2] have reported structural values for spiropentane, observed by means of electron diffraction. These values were used here, along with spectroscopic data quoted in Reference 3.

## Construction of Symmetry Coordinates

One cyclopropylene fragment of $C_{2v}$ symmetry has 15 normal modes of vibration distributed as

$$(C_{2v}) \quad 5\,a_1 + 3\,a_2 + 3\,b_1 + 4\,b_2 \,.$$

The $b_1$ and $b_2$ species designations depend on the orientation of cartesian axes.

The in-phase (+) and out-of-phase (−) vibrations for the two cyclopropylene fragments account for 30 normal modes of the spiropentane molecule of symmetry $D_{2d}$, which altogether has 33 normal modes according to

$$(D_{2d}) \quad 5\,A_1 + 3\,A_2 + 4\,B_1 + 5\,B_2 + 8\,E \,.$$

The excess 3 modes belong to $B_1 + E$.

In the present analysis the in-phase and out-of-phase combinations of cyclopropylene coordinates are used explicitly in the construction of the symmetry coordinates for spiropentane. The correlations between the symmetry species of the $C_{2v}$ and $D_{2d}$ point groups are deduced.

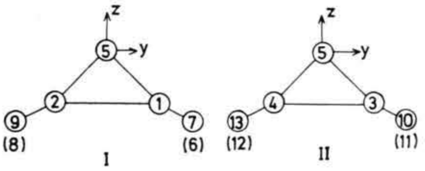

Fig. 1. Cyclopropylene ($C_3H_4$) fragments (I and II) with symmetry $C_{2v}$: Numbering of atoms and orientation.

Figure 1 shows the individual orientations of the two cyclopropylene fragments I and II, which are consistent with the symmetric structure given above. A complete set of independent coordinates for the vibrations of fragment I is given in the following, while numbering of atoms and definition of valence coordinates are given in Figure 2.

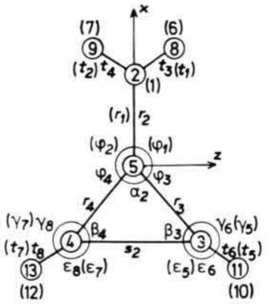

Fig. 2. Spiropentane molecular model; symmetry $D_{2d}$. Valence coordinates are indicated.

$$C_1{}^{\mathrm{I}}(a_1) = 2^{-1/2}(r_1 + r_2)$$
$$C_2{}^{\mathrm{I}}(a_1) = s_1$$
$$C_3{}^{\mathrm{I}}(a_1) = \tfrac{1}{2}(t_1 + t_2 + t_3 + t_4)$$
$$C_4{}^{\mathrm{I}}(a_1) = \tfrac{1}{2}(RT)^{1/2}(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)$$
$$C_5{}^{\mathrm{I}}(a_1) = \tfrac{1}{2}(ST)^{1/2}(\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4)$$
$$C_1{}^{\mathrm{I}}(a_2) = \tfrac{1}{2}(t_1 - t_2 - t_3 + t_4)$$
$$C_2{}^{\mathrm{I}}(a_2) = \tfrac{1}{2}(RT)^{1/2}(\gamma_1 - \gamma_2 - \gamma_3 - \gamma_4)$$

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$$
\begin{aligned}
C_3{}^{\mathrm{I}}(a_2) &= \tfrac{1}{2}(ST)^{1/2}(\varepsilon_1-\varepsilon_2-\varepsilon_3+\varepsilon_4)\\
C_1{}^{\mathrm{I}}(b_1) &= \tfrac{1}{2}(t_1-t_2+t_3-t_4)\\
C_2{}^{\mathrm{I}}(b_1) &= \tfrac{1}{2}(RT)^{1/2}(\gamma_1-\gamma_2+\gamma_3-\gamma_4)\\
C_3{}^{\mathrm{I}}(b_1) &= \tfrac{1}{2}(ST)^{1/2}(\varepsilon_1-\varepsilon_2+\varepsilon_3-\varepsilon_4)\\
C_1{}^{\mathrm{I}}(b_2) &= 2^{-\frac{1}{2}}(r_1-r_2)\\
C_2{}^{\mathrm{I}}(b_2) &= \tfrac{1}{2}(t_1+t_2-t_3-t_4)\\
C_3{}^{\mathrm{I}}(b_2) &= \tfrac{1}{2}(RT)^{1/2}(\gamma_1+\gamma_2-\gamma_3-\gamma_4)\\
C_4{}^{\mathrm{I}}(b_2) &= \tfrac{1}{2}(ST)^{1/2}(\varepsilon_1+\varepsilon_2-\varepsilon_3-\varepsilon_4)
\end{aligned}
$$

The corresponding set for fragment II is obtained by taking the analogous expressions. Thus, for instance $C_1{}^{\mathrm{II}}(a_1)=2^{-\frac{1}{2}}(r_3+r_4)$, $C_2{}^{\mathrm{II}}(a_1)=s_2$, $C_3{}^{\mathrm{II}}(a_1)=\frac{1}{2}(t_5+t_6+t_7+t_8)$, etc.

The in-phase and out-of-phase vibrations of spiropentane are defined by the symmetrical $(+)$ and antisymmetrical $(-)$ normalized combinations, respectively, of corresponding $C_i{}^{\mathrm{I}}$ and $C_i{}^{\mathrm{II}}$ coordinates. Thus, for instance

$$
\begin{aligned}
S_i(A_1) &= 2^{-1/2}[C_i{}^{\mathrm{I}}(a_1)+C_i{}^{\mathrm{II}}(a_1)]\ ;\\
S_i(B_2) &= 2^{-1/2}[C_i{}^{\mathrm{I}}(a_1)-C_i{}^{\mathrm{II}}(a_1)]\ .
\end{aligned}
$$

These expressions also indicate that $a_1(+)$ and $a_1(-)$ are correlated with $A_1$ and $B_2$, respectively. Separate correlations with degenerate coordinates of the $E$ species ($E_a$ and $E_b$) may be achieved if these coordinates are oriented properly. Figure 3 indicates the chosen orientation of the $a$ and $b$ coordinates. Figure 4 shows a complete scheme of the correlations in question. The coordinates chosen in accord with the scheme must also be provided with mutually correct signs in order to fulfil the requirements. In the present case one finds

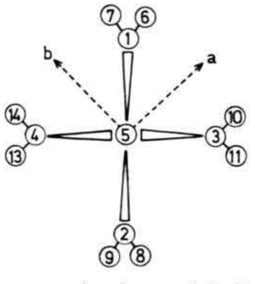

Fig. 3. Spiropentane molecular model: Orientation of the $a$ and $b$ coordinates of species $E$.

$$
S_a(E)=\begin{cases}2^{-1/2}[C^{\mathrm{I}}(b_1)+C^{\mathrm{II}}(b_1)]\ ,\\ 2^{-1/2}[C^{\mathrm{I}}(b_2)+C^{\mathrm{II}}(b_2)]\ ;\end{cases}
$$

$$
S_b(E)=\begin{cases}2^{-1/2}[C^{\mathrm{I}}(b_1)-C^{\mathrm{II}}(b_1)]\ ,\\ 2^{-1/2}[-C^{\mathrm{I}}(b_2)+C^{\mathrm{II}}(b_2)]\ .\end{cases}
$$

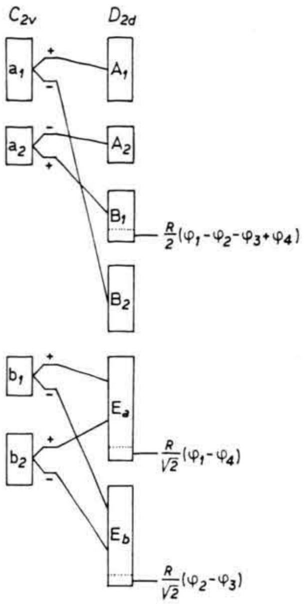

Fig. 4. Correlation between vibrational model of the $C_{2v}$ cyclopropylene fragments and the $D_{2d}$ spiropentane molecule.

Three additional coordinates are not accounted for by the correlations discussed above. They describe the mutual deformations (twisting and rocking) between the two cyclopropylene rings. The corresponding symmetry coordinates, expressed in terms of $\Phi$ bendings, are included on Figure 4.

## Force Constants

The analysis started with a very simple force field represented by a 44-dimensional diagonal F matrix with the following force constant values:

$$
f_r=f_s=4.15\,,\quad f_t=4.90\,,\quad f_\alpha=f_\beta=0.40\,,
$$
$$
f_\gamma=f_\delta=f_\varepsilon=0.30\,,\quad f_\Phi=0.20\,.
$$

all in mdyne/Å. In spite of the extreme simplicity of the initial force field we found a general qualitative agreement between the calculated and observed frequencies. Thus it gave a very good starting point for a further evaluation of the symmetry force constants.

As the next step in the analysis we considered the molecule as a combination of the two fragments of cyclopropylene in the way illustrated above in the construction of the symmetry coordinates. Interaction force constants between the two parts of the molecule were neglected except for the $r$-stretchings. In this case a strong coupling between the vibrations is to be expected. With the aid of Fig. 4 we assumed identical symmetry force constants for species $A_1$ and $B_2$ with the exception of $F_{11}$, which is the principal $r$ stretching force constant. Symmetry force constants of $B_1$ are equal to those of $A_2$ with the necessary addition caused by the $\Phi$ coordinate. Species $E$ can be regarded as consisting of three different parts (one from $b_1$, one from $b_2$ and the last caused by the $\Phi$ bendings) with no coupling inbetween. The frequencies calculated with this force field 2 (cf. Table 1) seem to verify the observed frequencies reported by Sverdlov et al.[3] and also generally support those frequencies given in parentheses therein. According to our results the $\nu_4$ bending frequency of $A_1$ should be expected to be higher than the corresponding one of $B_1(\nu_{11})$ in contrast to the suggestion of Sverdlov. An interchange of $\nu_4$ and $\nu_{11}$ was shown to influence the force constants only to a small degree and lead to negligible differences in the mean amplitudes. Hence we decided to maintain the assignment from Sverdlov et alias[3]. It should be mentioned that this final result fill out missing frequencies and partly disagree with the excellent but rather old spectroscopic work on spiropentane by Cleveland, Murray and Galloway[4]. These authors admit that there are unsolved problems in their assignment and mention that a normal coordinate analysis would be very useful to resolve some of these dubious points.

Table 1. Spiropentane. Calculated and observed[a] frequencies (in $\mathrm{cm}^{-1}$) with potential energy distribution (P.E.D.).

| Preliminary calculated Species | Preliminary calculated Force field 1[b] | Preliminary calculated Force field 2[c] | Finally calc. and observed | P.E.D.[d] |
|---|---|---|---|---|
| $A_1$: | 2950 | 2989 | 2991 | $0.98\ t$ |
| | 1567 | 1444 | 1461 * | $0.38\ \varepsilon+0.32\ \gamma+0.19\ s$ |
| | 1113 | 1025 | 1033 | $0.66\ s+0.20\ r$ |
| | 796 | 974 | 942 * | $0.44\ \gamma+0.36\ \varepsilon+0.16\ s$ |
| | 535 | 607 | 581 | $0.62\ r+0.19\ \gamma+0.16\ \varepsilon$ |
| $A_2$: | 3057 | 3069 | 3076 * | $0.99\ t$ |
| | 1191 | 1037 | 1030 * | $0.95\ \varepsilon+0.77\ \gamma$ |
| | 654 | 943 | 904 * | $0.45\ \gamma+0.26\ \varepsilon$ |
| $B_1$: | 3058 | 3072 | 3065 | $0.99\ t$ |
| | 1199 | 1055 | 1060 * | $1.04\ \varepsilon+0.79\ \gamma$ |
| | 654 | 944 | 982 * | $0.48\ \gamma+0.21\ \varepsilon$ |
| | 194 | 270 | 270 * | $0.96\ \Phi$ |
| $B_2$: | 2951 | 2987 | 2985 | $0.98\ t$ |
| | 1677 | 1462 | 1430 | $0.73\ r+0.27\ \gamma$ |
| | 1425 | 1383 | 1397 | $0.41\ \varepsilon+0.24\ r$ |
| | 1092 | 1008 | 993 | $0.92\ s+0.25\ \gamma$ |
| | 656 | 825 | 870 | $0.48\ \varepsilon+0.41\ \gamma$ |
| $E$: | 3049 | 3050 | 3050 | $1.00\ t'$ |
| | 2943 | 2935 | 2935 | $0.99\ t''$ |
| | 1497 | 1430 | 1430 | $0.43\gamma''+0.34\ \varepsilon''$ |
| | 1179 | 1189 | 1151 | $0.46\ \gamma'+0.41\ r$ |
| | 994 | 1028 | 1053 | $0.42\varepsilon'+0.31\ r+0.18\ \gamma'$ |
| | 774 | 893 | 896 | $0.4\ \gamma''+0.41\ \varepsilon''+0.22\ \varepsilon'$ |
| | 662 | 769 | 778 | $0.33\ \gamma'+0.26\ \varepsilon'$ |
| | 334 | 308 | 305 | $0.90\ \Phi$ |

[a] From Ref. 3. [b] Diagonal force field. [c] Neglecting interaction between rings except for the main $r$ stretchings. [d] Terms below 0.15 are neglected. * Given by Sverdlow et al.[3] in parentheses.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 5.350 | | | | | | | | Species $A_1$ |
| 2 | −0.786 | 4.704 | | | | | | | |
| 3 | −0.070 | −0.059 | 5.014 | | | | | | |
| 4 | −0.048 | −0.199 | 0.013 | 0.471 | | | | | |
| 5 | 0.136 | 0.136 | 0.028 | 0.046 | 0.050 | | | | |
| 1 | 4.949 | | | | | | | | Species $A_2$ |
| 2 | −0.027 | 0.440 | | | | | | | |
| 3 | −0.019 | −0.170 | 0.359 | | | | | | |
| 1 | 4.906 | | | | | | | | Species $B_1$ |
| 2 | −0.029 | 0.505 | | | | | | | |
| 3 | −0.015 | −0.217 | 0.401 | | | | | | |
| 4 | −0.001 | 0.001 | −0.001 | 0.395 | | | | | |
| 1 | 3.768 | | | | | | | | Species $B_2$ |
| 2 | −1.102 | 4.731 | | | | | | | |
| 3 | −0.082 | −0.074 | 4.997 | | | | | | |
| 4 | 0.083 | −0.250 | 0.016 | 0.500 | | | | | |
| 5 | 0.129 | 0.158 | 0.030 | −0.001 | 0.538 | | | | |
| 1 | 4.901 | | | | | | | | Species $E$ |
| 2 | 0.003 | 0.336 | | | | | | | |
| 3 | −0.005 | −0.055 | 0.401 | | | | | | |
| 4 | −0.013 | −0.053 | −0.029 | 5.478 | | | | | |
| 5 | −0.001 | −0.003 | −0.002 | 0.004 | 4.874 | | | | |
| 6 | −0.001 | −0.003 | 0.001 | −0.031 | 0.007 | 0.508 | | | |
| 7 | −0.002 | −0.005 | −0.006 | −0.077 | 0.005 | 0.073 | 0.469 | | |
| 8 | 0.001 | 0.002 | 0.001 | 0.003 | 0 | 0 | 0.002 | 0.159 | |

Table 2. Symmetry force constants (in mdyne/Å) for spiropentane.

Table 3. Mean amplitudes of vibration, $\boldsymbol{u}$ (in Å units) for spiropentane

| Distance type (i−j) | | (Equil. dist in Å) | **u** spectr. 0 K | 298 K | **u** electr. diff. Ref. 2 |
|---|---|---|---|---|---|
| C−H | (1−6) | (1.091) | 0.0777 | 0.0777 | 0.072 |
| C−C | (1−2) | (1.519) | 0.0498 | 0.0501 | 0.047 |
| C−C | (1−5) | (1.469) | 0.0483 | 0.0488 | 0.047 |
| C...C | (1−3) | (2.736) | 0.0648 | 0.0734 | 0.068 |
| C...H | (1−8) | (2.225) | 0.1077 | 0.1085 | 0.115 |
| C...H | (5−6) | (2.193) | 0.1071 | 0.1081 | 0.115 |
| C...H | (1−10) | (3.073) | 0.1446 | 0.1588 | 0.136 |
| C...H | (1−11) | (3.505) | 0.1193 | 0.1255 | 0.136 |
| H...H | (6−7) | (1.874) | 0.1240 | 0.1241 | |
| H...H | (6−8) | (2.474) | 0.1698 | 0.1715 | |
| H...H | (6−9) | (3.104) | 0.1366 | 0.1377 | |
| H...H | (6−10) | (3.127) | 0.2157 | 0.2406 | |
| H...H | (6−11) | (3.797) | 0.1823 | 0.1981 | |
| H...H | (6−13) | (4.365) | 0.1437 | 0.1461 | |

Finally the force constants were adjusted to fit exactly the adopted assignment. Potential energy distribution was calculated and is given in Table 1. Final symmetry force constants are found in Table 2.

## Mean Amplitudes Vibration

Table 3 shows the mean amplitudes of vibration ($\boldsymbol{u}$) at absolute zero and 298 K. Included in the table are also $\boldsymbol{u}$ values from electron diffraction[2]. We judge the agreement between observed and calculated mean amplitudes of vibration to be very satisfactory.

*Acknowledgement:* The authors are indebted to Professor S. J. Cyvin for valuable discussions.

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