Analysis of Several High-Resolution Infrared Bands of Spiropentane, C₅H₈

A. Maki^a, J.E. Price^b, Jared Harzan^b, J.W. Nibler^{b,**},

A. Weber^c, T. Masiello^d, and T.A. Blake^e

^a15012 24th Ave., S.E, Mill Creek, WA, 98012

^bDepartment of Chemistry, Oregon State University, Corvallis, OR, 97332-4003

^cSensor Science Division, National Institute of Standards and Technology,
Gaithersburg, MD 20899

^dDepartment of Chemistry & Biochemistry, 226 Science Building, Eastern Washington
University, Cheney, WA 99004

^ePacific Northwest National Laboratory, P.O. Box 999, Mail Stop K3-61, Richland, WA
99352

Number of text pages: 18

Number of Tables: 5

Number of Figures: 4

** Corresponding author.

E-mail address: Niblerj@chem.orst.edu

FAX: +1- 541-737-2062

Keywords: Spiropentane; High-resolution infrared spectrum; Rovibrational constants; DFT study;
Anharmonic frequencies

Abstract

The high-resolution infrared absorption spectrum of spiropentane (C_5H_8) has been measured from 200 to 4000 cm^{-1} , and a detailed analysis is presented for eight bands in the region from 700 to 2200 cm^{-1} . Two fundamental perpendicular bands were analyzed, ν_{22} and ν_{24} near 1050 and 780 cm^{-1} , respectively, along with two fundamental parallel bands, ν_{14} and ν_{16} near 1540 and 990 cm^{-1} , respectively. Two other fundamentals, ν_{17} and ν_{23} , are seen as intense overlapping bands near 880 cm^{-1} and are Coriolis-coupled, producing a complex mixture in which only *P*-branch transitions could be tentatively assigned for ν_{17} . In addition, three binary combination bands were fit at about 1570, 2082, and 2098 cm^{-1} which are assigned as either $2\nu_{24}$ or $\nu_5+\nu_{16}$ in the first case, $\nu_4+\nu_{22}$ in the second case, and $2\nu_{22}$ in the latter case. The two *l*-type resonance constants, q^+ and q^- , were determined for each of the two perpendicular fundamentals ν_{22} and ν_{24} . Those two constants were also responsible for splittings observed in the $K = 3$ levels of ν_{24} . For the ground state the order of the split $K = 2$ B_1/B_2 levels has been reversed from that reported previously, based on the measurements and assignments for the ν_{24} band. Rovibrational parameters deduced from the analyses are compared with those obtained from density functional Gaussian calculations at the anharmonic level.

1. Introduction

As the simplest bicyclic ring compound, the structure and physical properties of spiropentane are of special interest. The ring strain in spiropentane (265 kJ mol^{-1}) is more than twice that of cyclopropane (115 kJ mol^{-1}), the excess being attributed to the spiro-arrangement about the central carbon.[1] Despite this strain, spiropentane is remarkably stable up to temperatures of about 350°C . Spiropentane is a symmetric top and it, along with allene and cyclobutane, are the only molecules of molecular symmetry D_{2d} known to us for which high resolution vibration-rotation spectra have been analyzed to obtain accurate molecular constants. Such information is particularly useful in assessing the merits of quantum calculations of the anharmonic potential function using programs such as Gaussian.

The infrared spectrum of spiropentane was first measured by Murray and Stevenson [2]. Subsequently, Cleveland et al. [3] and then Burns and McGavin [4] reported the results of infrared and Raman spectral measurements. Gaussian calculations were used by Schaad and Jarzecki [5] to verify the assignment of the fundamental vibrational wavenumbers and similar calculations were extended in a recent paper from this laboratory [6]. In that study of the high-resolution infrared spectrum of spiropentane, partial analyses of several fundamental bands and two combination bands were used to give ground state combination-differences to determine accurate values for the rotational constants of spiropentane in the ground state. We have now extended those analyses and added the analysis of another fundamental band, a perpendicular band, ν_{22} , near 1052 cm^{-1} . Theoretical ν_0 and intensity values for the fundamentals, along with mode numbering, symmetry, and assigned values [4] are given in our previous paper [6].

The spectrum of spiropentane is cluttered with hot band transitions due to the two low wavenumber fundamental bands, ν_{12} at about 300 cm^{-1} and ν_{25} at about 308 cm^{-1} . At room temperature about 61% of the molecules are in the ground state while in sum about 14% are in the two lowest vibrational states, with the remaining 25% in other vibrational states. Consequently, the spectrum will generally have many unassigned transitions. The rovibrational analysis of the low K levels for degenerate states in spiropentane is further complicated by splittings produced by *two* l -resonance constants q^+ and q^- (only one such term, q^+ , occurs for symmetric tops with three-fold symmetry). In our earlier paper [6] a very small splitting of the K

= 2 levels was also observed for one parallel band, ν_{16} , and used to determine the Δ_2 splitting constant in the ground state. In the present work the larger l -resonance splitting of the $kl = \pm 1$ and $kl = \pm 3$ levels of two degenerate fundamentals, ν_{22} and ν_{24} , was observed. From the analysis of these splittings it was necessary to revise the analysis of the splitting for the ground state and for ν_{16} . These new measurements did not make a significant change to the absolute value of the Δ_2 splitting constant for the ground state, but the order of the B_1 and B_2 levels has been changed.

2. Experimental details

The synthesis of our sample of spiropentane was described in the earlier paper [6]. The high-resolution infrared spectra were measured on the Bruker IFS 125HR Fourier transform spectrometer¹ located at the Pacific Northwest National Laboratory. In recording the spectra a Globar light source, KBr beamsplitter, and either MCT or InSb detectors were used. The spectrometer and optical path outside of the absorption cell was evacuated. The sample was contained in a White-type absorption cell with a path length of 12.8 m. Sample pressures between 150 and 16 Pa (1.1 and 0.12 torr) were used, depending on the intensity of the band being measured. Measurements were made from 200 to 4000 cm^{-1} with a resolution of about 0.002 cm^{-1} . No transitions below 750 cm^{-1} or above 2100 cm^{-1} were fit, because no regular patterns were discerned among the bands that were strong enough to be measured.

The wavenumber scale for the spectra was based on CO_2 [7] and N_2O [8] gas reference samples measured immediately before or after the spiropentane spectrum was recorded. The calibration correction was typically less than 0.0002 cm^{-1} and it is believed that the absolute wavenumber accuracy is comparable.

As an example of the spectra obtained, Fig. 1 displays a high-resolution scan of the 780 cm^{-1} perpendicular band ν_{24} . As shown at the top of the figure, the Gaussian calculations indicate that this mode is predominantly a rocking motion of the CH_2 groups. The trace at the bottom shows the spectrum as calculated with the constants given in this paper.

¹Certain commercial equipment, instruments, and materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendations or endorsements by the National Institute of Standards and Technology or the Pacific Northwest National Laboratory, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

3. Band Analyses

3.1 Rovibrational level expressions

The analysis of the spectra used the same basic symmetric-top least-squares fitting program that was used for the earlier paper [6]. Since we have used no off-diagonal matrix elements that connect the A and B rotational levels, each matrix only includes rovibrational levels with either A, B, or E symmetry. We give here all the basic equations that were used in the present work.

Neglecting interaction terms, the total rovibrational term value expression is given by

$$E(v_m, v_n, \dots, l_m, l_n, \dots, k, J) = G(v_m, v_n, \dots, l_m, l_n, \dots) + F_v(J, k, l_m, l_n, \dots). \quad (1)$$

All constants and terms are given in wavenumber units (cm^{-1}). For convenience we have chosen to base the vibrational term value expression, $G(v, l)$, on the ground state so that $G(0, 0) = G_0 = 0 \text{ cm}^{-1}$. If we then use G_0 for the zero point energy, the customary expression for the total vibrational term value becomes

$$G_0 + G(v, l) = \sum \omega_i (v_i + \frac{1}{2} d_i) + \sum_{i \leq j} x_{ij} (v_i + \frac{1}{2} d_i) (v_j + \frac{1}{2} d_j) + \sum_{i \leq i'} x^{ii'} l_i l_{i'} + \dots \quad (2)$$

If there is no vibrational resonance to affect the band center, then the usual symbol that stands for the band center, v_0 , is equivalent to $G(v, l) - G(v, l)''$.

The last term in Eq. (1) is the expression for the rotational term value. In its most general form, this standard energy (or term value) expression describing the rotational levels of a vibrational state of quantum number v is

$$\begin{aligned} F_v(J, k, l_i) = & B_v J(J+1) + (A_v - B_v) K^2 - \sum k l_i [2A \zeta_i - \eta_{iJ} J(J+1) - \eta_{ik} K^2 - \eta_{iJJ} J^2(J+1)^2 \\ & - \eta_{iJK} J(J+1) K^2 - \eta_{iKK} K^4] - D_v J^2(J+1)^2 - D_{vJK} J(J+1) K^2 - D_{vK} K^4 \\ & + H_{vJ} J^3(J+1)^3 + H_{vJK} J^2(J+1)^2 K^2 + H_{vKJ} J(J+1) K^4 + H_{vK} K^6 + \text{splitting terms.} \end{aligned} \quad (3)$$

In this paper, as is usual, lower case rotational quantum numbers are signed numbers while

absolute values are used for upper case quantum numbers. Here, the rotational constants are given by

$$B_v = B_e - \sum_i \alpha_i^B (v_i + 1/2 d_i) + \dots, \quad (4)$$

with $-\alpha_i^B = B_i' - B_i'' = \Delta B$ and similar expressions describing the other rotational constants, A_v , D_{vJ} , etc. The D , H and η terms account for centrifugal distortion effects. For the ground vibrational state and for all other vibrational states with $l = 0$ treated in this paper, the splitting term is given by

$$\text{splitting} = \pm \delta_{2K} \Delta_{2v} [J(J+1)][J(J+1) - 2] \quad (5)$$

which only affects the $K = 2$ rotational levels. The first factor on the right hand side of Eq. (5) is the Kronecker delta symbol, δ_{2K} , which is zero if $K \neq 2$; the second symbol, Δ_{2v} , is the splitting constant which is very small, on the order of 10^{-9} cm^{-1} or less. Its determination requires the observation of transitions with high J values, which is seldom the case. The only states that required such a splitting term were the ground state and v_{16} . For all other states the measurements did not extend to high enough values of J to enable a determination of that splitting constant.

Since spiropentane has D_{2d} symmetry, for vibrational states with $l = 1$, both the $kl = +1$ and the $kl = -1$ levels are split by l -type resonance constants q^+ and q^- whose determination requires the use of the off-diagonal matrix elements

$$\begin{aligned} W_{2,2} &= \langle v_t, J, k, l_t | H | v_t, J, k \pm 2, l_t \pm 2 \rangle \\ &= 1/4 [q_t^+ + q_{tJ}^+ J(J+1) + q_{tK}^+ (k^2 + (k \pm 2)^2)] [(v_t + 1)^2 - (l_t \pm 1)^2]^{1/2} \\ &\quad \times [J(J+1) - k(k \pm 1)]^{1/2} [J(J+1) - (k \pm 1)(k \pm 2)]^{1/2} \end{aligned} \quad (6)$$

and

$$\begin{aligned} W_{2,-2} &= \langle v_t, J, k, l_t \pm 2 | H | v_t, J, k \pm 2, l_t \rangle \\ &= 1/4 [q_t^- + q_{tJ}^- J(J+1) + q_{tK}^- (k^2 + (k \pm 2)^2)] [(v_t + 1)^2 - (l_t \pm 1)^2]^{1/2} \\ &\quad \times [J(J+1) - k(k \pm 1)]^{1/2} [J(J+1) - (k \pm 1)(k \pm 2)]^{1/2}. \end{aligned} \quad (7)$$

Those matrix elements also result in a splitting of the $kl = +3$ and $kl = -3$ levels, although this is much smaller than that for the $kl = +1$ and $kl = -1$ levels.

One degenerate state, v_{24} , required an additional matrix element, $W_{4,0}$, to improve the fit of the $K = 1$ levels beyond the splitting provided by the above terms.

$$W_{4,0} = \langle v, J, k, l | H | v, J, k \pm 4, l \rangle = w_{4,0} [J(J+1) - k(k \pm 1)]^{1/2} [J(J+1) - (k \pm 1)(k \pm 2)]^{1/2} \\ \times [J(J+1) - (k \pm 2)(k \pm 3)]^{1/2} [J(J+1) - (k \pm 3)(k \pm 4)]^{1/2}, \quad (8)$$

where $w_{4,0}$ is an off-diagonal splitting constant.

The sign of the q^+ splitting constant follows the convention discussed by Cartwright and Mills [9] and used by others in the analysis of the spectrum of allene [10,11] and by us in previous work on D_{3h} symmetric top molecules such as propellane [12, 13]. This convention was chosen by Cartwright and Mills to achieve agreement between experimental and theoretical signs for q^+ for symmetric tops of C_{3v} symmetry and, as applied to molecules of D_{2d} symmetry, with q^+ defined by our Eq. 6, is that q^+ is positive if the B_1 rovibrational level is above the B_2 level for even J values, and the reverse for odd J values.² These authors explicitly avoid a choice of convention for q^- , but an operational choice was made for allene in Reference 11 in which q^- is positive for even J values if $A_1 > A_2$. We have adopted this choice here. If sufficiently separated, transitions to both the A_1/A_2 levels are visible and can be identified because the intensity ratio should be that of the nuclear spin weights, 76/60. Similarly, transitions to B_1/B_2 split levels will have a 76/60 intensity ratio. More details regarding the ordering and signs of the A_1/A_2 and B_1/B_2 pairs are given in the discussion of each band.

3.2 Ground state rotational constants

In our earlier paper on spiropentane [6] the ground state rotational constants were given based on the combination-differences then available. The present work has added more than 1500 ground state combination-differences so a new fit has been made that includes all the

²The $W_{2,2}$ matrix element in reference [9] has a leading negative sign whereas our Eq. (6) does not, nor does the $W_{2,2}$ element defined in references [10,11]. To compensate for this, the level ordering convention given above is the opposite of that given in reference [9]; thus in both cases q^+ has the same sign and can be compared to the theoretical expression given in [9].

currently available data. Despite this increase in the data set size, the sextic centrifugal distortion H constants remained poorly determined and hence were fixed at zero values. The results are given in Table 1 and these ground state constants were used in all the fits in the present work. The new ground state constants are only slightly different from the earlier values but are expected to be more accurate. The main difference is the splitting constant Δ_2 , for which a more accurate value was determined by the current analysis of the ν_{24} band and for which the positive sign agrees with the theoretical value if one uses the convention adopted for allene in Reference 11. A summary of our convention for order of levels for positive splitting constants is thus

	$\frac{q^+ > 0}{B_1 > B_2}$	$\frac{q^- > 0}{A_1 > A_2}$	$\frac{\Delta_2 > 0}{B_1 < B_2}$
J even	$B_1 > B_2$	$A_1 > A_2$	$B_1 < B_2$
J odd	$B_1 < B_2$	$A_1 < A_2$	$B_1 > B_2$

3.3 The ν_{24} 780 cm^{-1} perpendicular band

The lowest wavenumber band studied in this paper is the ν_{24} perpendicular band centered at 779.126 cm^{-1} . No other vibrational energy level is within 90 cm^{-1} of ν_{24} and so it is found, as expected, to be free of any perturbations. As seen in Figure 1, the spectrum is very crowded but the analysis was nonetheless straight-forward; Table 2 gives the constants found from a fit of over 5700 ν_{24} transitions. Of special interest were the three important splitting constants, q^+ and q^- for ν_{24} and Δ_2 for the ground state. From the fit of the transition wavenumbers alone it is not possible to determine the signs of any of these splitting parameters, but these can be obtained with the sign conventions described above, in combination with intensity considerations discussed below. Included in the fit were all the constants given in Eqs. (6) and (7) as well as the small $w_{4,0}$ constant given in Eq. (8). The $w_{4,0}$ constant is similar to Δ_2 for the ground state (both involve the $J_+^4 + J_-^4$ operator), but for a degenerate state $w_{4,0}$ has its greatest effect on the $K = 1$ levels. Once the signs of both q^+ and q^- are known then the sign of $w_{4,0}$ is given by the fit.

The B_1/B_2 splitting for the $kl = +1$ levels of ν_{24} is caused by the q^+ parameter via the $W_{2,2}$ off-diagonal matrix element defined by Eq. 6. The observed transitions to those levels all originate from the $K = 0$ levels of the ground state. Therefore, the correct order of the upper state B_1/B_2 levels is determined by the fact that the lower state $K = 0$ levels are A_1 for even J -values and A_2 for odd J -values and the only allowed infrared rovibrational transitions are $B_1 \leftrightarrow A_1$ or $B_2 \leftrightarrow A_2$ or $E \leftrightarrow E$. The analysis shows that the $\Delta J = 0$ Q -transitions all go to the lower of the two

levels for $kl = +1$ while the $\Delta J = \pm 1$ P - and R -transitions all go to the upper level. For this reason, without resorting to any intensity measurements, we have given q^+ a *negative* sign to be consistent with the sign convention above.

Since the $kl = +1$ levels are coupled to the $kl = -3$ levels through the q^- constant, the latter levels should show a significant splitting with a B_1/B_2 order the same as for the $kl = +1$ levels, regardless of the sign of q^- . That expectation is confirmed by the calculated values which agree with the observed transitions. Similarly the q^+ constant couples the $kl = -1$ levels to the $kl = +3$ levels, so that the ordering of the A_1 , A_2 levels is the same for $kl = -1$ and $kl = +3$ of v_{24} . (The $w_{4,0}$ constant is so small that it does not reverse that ordering for any of these cases).

From the splitting of the $kl = -1$ or $+3$ levels of v_{24} we can determine very accurate values for the magnitude of q^- but not its sign. Only by observing the relative intensities of the split transitions can we determine the ordering of the A_1/A_2 levels and therefore the sign of q^- . It is important to be able to compare the intensity of two lines that are adjacent so that the effects of noise or overlapping with other lines are minimized. The splittings of the rQ_2 transitions for $J > 28$ are convenient for this since, though small, the resultant doublets can be resolved, see Figure 2. As an example, consider the doublet for $J = 32$. Since we have accurate absolute values for q^+ and q^- we can calculate that, for instance, the splitting of the $kl = +3$ levels for $J = 32$ is 0.0014 cm^{-1} . We also have accurate values for Δ_2 but not its sign. The calculated splitting of the $J = 32$, $K = 2$ levels for the ground state is 0.0026 cm^{-1} . The observed splitting of the ${}^rQ_2(32)$ transition is 0.0038 cm^{-1} which is approximately the sum of the upper and lower state splittings. As can be seen for ${}^rQ_2(32)$ in Fig. 2, the more intense doublet member, which must be the $A_1 \leftarrow B_1$ transition, must begin at the lower of the ground state split levels and go to the upper of the v_{24} levels. Since the B_1/B_2 levels must be reversed if J is raised or lowered by one unit, then the splitting of the corresponding ${}^rR_2(31)$ and ${}^rP_2(33)$ transitions should be given by the *difference* rather than the sum of the lower and upper state splittings, making the splitting quite small. This is consistent with the fact that we do not discern any indication of splitting of the ${}^rR_2(31)$ and ${}^rP_2(33)$ transitions.

A second example is provided by the odd- J ${}^rQ_2(41)$ transitions (not shown), which seem to be free of overlapping and have a separation of 0.01346 cm^{-1} , which is equal to the sum of the calculated upper state splitting, 0.00647 cm^{-1} , and the lower state splitting, 0.00694 cm^{-1} . As for the odd- J ${}^rQ_2(29)$ shown in Fig. 2, the lower component is stronger than the upper component,

the reverse of the order for even- J transitions. The corresponding splitting of the 1R_2 and 1P_2 transitions is again small and is only observed at much higher J -values.

The splittings of the pP_2 , pR_2 , and pQ_2 transitions to $kl = -1$ levels are much larger and, although the lines are too widely-spaced and too badly overlapped to enable us to make good comparisons of the relative intensities, the splitting values are consistent with level orders deduced above. For example, the upper state splitting for $J = 32$ is calculated to be 0.5739 cm^{-1} so that the observed splitting of the ${}^pQ_2(32)$ transitions should be 0.5764 cm^{-1} ; the observed splitting is 0.5772 cm^{-1} . For the ${}^pR_2(31)$ transitions the measured splitting should be slightly smaller than 0.5739 and is observed to be 0.5721 cm^{-1} . For ${}^pP_2(33)$ the observed splitting is also smaller, 0.5732 cm^{-1} . Similar comparisons can be made for higher J -values so that we are confident of the assignments and conclusions.

The result of the above observations is the conclusion that for the same J -values the ordering of the B_1/B_2 levels for $K = 2$ in the ground state must be opposite to the ordering of the A_1/A_2 levels for $kl = -1$ of ν_{24} . Therefore Δ_2 should be *positive* and q^- should also be *positive*. Figure 3 summarizes the relative ordering of the energy levels for the ground state and for ν_{24} . Although the figure is not to scale, the figure shows the correct relative ordering of the A_1/A_2 and B_1/B_2 split levels. Only a few $\Delta J = 0$ transitions are shown in the figure but, of course, $\Delta J = \pm 1$ transitions were also observed.

3.4 The $\nu_{22} 1051 \text{ cm}^{-1}$ perpendicular band

Another fundamental band that appears to be relatively free of perturbations is ν_{22} centered at 1051.36 cm^{-1} . There are, however, many unassigned lines in this region and the density of lines is such that almost all lines are blended with other lines. It is predicted that ν_4 , and possibly ν_3 , should be close to ν_{22} but the spectrum does not show any obvious effects due to ν_4 or any other nearby level.

As was the case for ν_{24} the B_1/B_2 splitting of the $kl = +1$ levels is rather large. The fact that the 1Q_0 transitions all go to the upper $kl = +1$ level while the 1P_0 and 1R_0 transitions go to the lower $kl = +1$ levels means that the splitting constant, q^+ , must be *positive*. That is opposite to what was found for ν_{24} . This goes along with, but is probably not related to, the reversal of the sign of $A\zeta$.

The A_1/A_2 splitting of the $kl = -1$ levels is quite small and the overlapping with other

transitions is so severe that it is not possible to determine the sign of q^- from intensity measurements. However, since we know the order of the ground state $K = 2$ levels, the order of the $kl = -1$ levels of ν_{22} is determinable from measured transitions with $J > 28$. The PQ_2 transitions are too badly overlapped to allow a good determination of the splitting, but that is not the case for a few PP_2 and PR_2 transitions. Those transitions all show that the splitting of the transitions is smaller than the splitting of the upper state, hence for a given J the order of the A_1/A_2 levels for $kl = -1$ of ν_{22} must be opposite to the order of the B_1/B_2 levels of the ground state. Therefore the sign of q^- must be opposite to the sign of Δ_2 for the ground state and is thus *negative*.

Because of the small value for the q^- constant, the splitting calculated for the $K = 3$ levels is too small to observe. Instead, the splitting of the RQ_2 , RP_2 , and RR_2 transitions must be primarily due to the splitting of the ground state $K = 2$ levels. The calculated splitting of those levels is on the order of 0.0092 cm^{-1} , compared with the observed splitting of 0.0094 cm^{-1} at the highest J -values observed, $J'' = 44$. In any case, those transitions are so badly overlapped with other transitions that intensity measurements cannot be used to independently verify the sign of q^- or the sign of the ground state Δ_2 constant. The constants are given in Table 2.

3.5 The revised analysis of the ν_{16} parallel band near 993 cm^{-1}

Since the analysis of the band near 780 cm^{-1} reverses the order of the split $K = 2$ levels for the ground state, we have reanalyzed the 993 cm^{-1} band. In the P -branch for the $K = 2$ transitions the splitting is much smaller than that due to the lower state alone. In addition, the transitions that are displaced to lower wavenumbers between $J'' = 50$ and $J'' = 56$ are stronger for odd J'' values and weaker for even J'' values, in agreement with the lower state ordering shown in Figure 3. The transitions involving higher J -values are less reliable since they are weaker.

It is significant that the splitting of the 4P_2 transitions is small, much less than the sum of the upper and lower state splittings that is predicted if the signs are identical for both states. The intensity pattern thus requires the upper state to have a splitting constant that is opposite in sign and smaller than that of the ground state. This sign reversal is not surprising because in going from the A_1 ground state to the $B_2 \nu_{16}$ state the product of the vibrational symmetry species and the rotational symmetry for the $K = 2$ rotational levels will reverse the order B_1 above (or below) B_2 to A_2 above (or below) A_1 , i.e. $B_2 \times B_1 = A_2$ and $B_2 \times B_2 = A_1$. Therefore one would expect that

for $K = 2$ of ν_{16} , the A_1 levels would be above the A_2 levels for even J . The important result is that there is no significant difference from the earlier analysis, except for the sign of Δ_2' , as shown by the constants given in Table 3.

3.6 The two parallel bands at 1539.5 and 1567.5 cm^{-1}

Two parallel bands are observed in the 1550 cm^{-1} region and, as seen in Figure 4, these have nearly the same intensity. The transitions involving the $K = 0, 1$, and 2 levels were not resolved for either band and both have many unexplained extra lines that may or may not be due to hot-band transitions. Only one fundamental band is expected, namely ν_{14} , and the Gaussian calculations favor assignment of the lower band as ν_{14} . The K -structure of the P - and R -branch features is condensed and only 450 transitions could be assigned, giving, however, a very good rms deviation value of 0.00040 cm^{-1} .

The assignment of the upper band is less clear and could be $\nu_5 + \nu_{16}$ (B_2) or $2\nu_{24}$ (A_1, B_1, B_2). A spectrum calculated in the first case (shown in Fig. 4) gives a good fit, although some band heading is seen in the R -branch at high J . If the upper state is $2\nu_{24}$, it would have to be the B_2 component with either $l = +2$ or $l = -2$ and it would be coupled to the other l components through l -type doubling matrix elements, as well as being coupled to ν_{14} through a vibrational resonance. In the fit of the upper band with this $2\nu_{24}$ assignment, the inclusion of a $\Delta k = \pm 2$, $\Delta l = \pm 2$ matrix element equivalent to a q^+ term was used to couple the $l = 0$ and $l = \pm 2$ levels. In addition, one should use a term equivalent to a q^- term to couple the B_1 and B_2 vibrational states, but that was not done because the data did not justify it. Despite this, the upper band fit was comparable to that obtained for the $\nu_5 + \nu_{16}$ assignment and both alternatives are included in Table 4. The simulated spectrum for $2\nu_{24}$ is not shown in Fig. 4, since it closely resembles that for shown for $\nu_5 + \nu_{16}$. The rms deviations are essentially identical for both assignments so experiment does not allow a choice of one over the other.

Theory offers some guidance here, as shown in Table 5. For ν_{14} , the theoretical ΔA and ΔB values are in good accord with experiment and the ν_0 value is also reasonable, since a Fermi resonance between the B_2 ν_{14} , $2\nu_{24}$ and $\nu_5 + \nu_{16}$ levels is expected, even though the wavenumber fits did not show evidence of such resonances. From the Gaussian calculations of level separations and the $\phi_{14,24,24}$ and $\phi_{5,14,16}$ cubic coupling terms, 39 and 11 cm^{-1} , respectively, the resonance of ν_{14} with $2\nu_{24}$ should be much more important than that with $\nu_5 + \nu_{16}$ and this would

compensate for the lower theoretical anharmonic intensity listed in table for $2\nu_{24}$ compared to $\nu_5+\nu_{16}$. The ΔA and ΔB values of the upper 1567.5 cm^{-1} band are about twice that of the lower 1539.5 cm^{-1} band. The theoretical and experimental ΔA and ΔB values for the upper state are in poorer agreement for the $\nu_5+\nu_{16}$ assignment and the very large ΔH values found for this assignment also favors the $2\nu_{24}$ assignment. Finally, though not analyzed, there is a weak Q -branch of a parallel band at about 1582.5 cm^{-1} and this is very close to the $\nu_5+\nu_{16}$ value of 1585 cm^{-1} that is predicted from theory. For these reasons, we favor the assignment of the 1567.5 cm^{-1} band as $2\nu_{24}$, but we caution that the constants given in Table 4 for this state should be regarded as fitting parameters for an incomplete model.

3.7 The two parallel bands near 2098 and 2145 cm^{-1}

Two parallel bands are observed in this region and the theoretical calculations predict only three B_2 states as possible upper state assignments in the range 2050 to 2200 cm^{-1} : $\nu_5+\nu_{14}$, $2\nu_{22}$, and $\nu_7+\nu_{11}$. The predicted parameters for each are shown in Table 5 and comparison of predicted intensities and the ΔA and ΔB values clearly favor the assignment of the more intense band centered at 2098.21 cm^{-1} as the B_2 component of $2\nu_{22}$.

The analysis and assignment of the higher 2145 cm^{-1} band is less certain. This band is very weak and the high- K features cannot be distinguished from the noise and clutter of hot band transitions. There is much structure in this region that is consistent with one or more perpendicular bands, but the analysis of this was not possible. However, a long series of P -branch-like parallel-band features extends from 2134 to 2142 cm^{-1} and a complementary series of R -branch-like features extends from 2149 to 2153 cm^{-1} . The low- J' features for each P and R -branch shade to higher wavenumbers as K increases while the high- J' features shade to lower wavenumbers, with the P - and R -branch features clearly sharpest for the $J' = 22$ transitions in both branches. This J' -assignment is consistent with the weak Q -branch feature whose band center appears to be at $2145.747\pm0.010\text{ cm}^{-1}$. The change in shading of the features suggests that there is a crossing point at $J' = 22$ for two interacting bands. We note that the structure of the band is quite similar to that of the ν_{17} band we have previously analyzed for bicyclopentane [15]. In that case the shape of the bicyclopentane band was found to be due to the x-y Coriolis interaction with the nearby degenerate fundamental ν_{11} .

A similar Coriolis interaction is expected between ν_7 (A_2) and ν_{21} (E) of spiropentane,

which are calculated to be only a few cm^{-1} apart. Because of that, we expect that the combination states $\nu_7+\nu_{11}$ and $\nu_{11}+\nu_{21}$ will also be coupled through a $\zeta_{7,21}$ Coriolis term, which will result in a band that looks very much like Fig. 3 in Reference 15 for bicyclopentane. For spiropentane, the theoretical value of $\zeta_{7,21}$ is 0.4, a value large enough that this the coupling term will be significant. As seen in Table 5, the ν_0 and intensities are consistent with assignment of the band as $\nu_7+\nu_{11}$ but the experimental value deduced for ΔB is negative ($-0.90 \times 10^{-3} \text{ cm}^{-1}$), versus a positive value ($+0.06 \times 10^{-3} \text{ cm}^{-1}$) from theory. Also, the shading of the Q -branch to lower wavenumbers would seem to require a negative value for ΔA , whereas the theoretical value is predicted to be positive.

The alternative assignment of the band is as $\nu_5+\nu_{14}$ (B_2) where a weak Coriolis interaction could also occur, with either $\nu_{11}+\nu_{21}$ or a $\nu_{16}+\nu_{21}$ (E) state at slightly higher energy. It may be significant that if the band is simply fitted as $\nu_5+\nu_{14}$, without any coupling, the sign disagreements for ΔA and ΔB disappear. The intensity predicted for this assignment is also slightly higher than for the $\nu_7+\nu_{11}$ choice. The predicted ν_0 value is 26 cm^{-1} lower than the observed band center however, but such a lowering could be a consequence of Fermi mixing of the two B_2 states. All in all, the fits are judged to slightly favor the $\nu_5+\nu_{14}$ assignment but this conclusion should be regarded as tentative.³

3.8 The perpendicular band near 2082 cm^{-1}

Buried in the P -branch region of the 2098 cm^{-1} parallel band is a series of Q -branch-like lines that seem to belong to a perpendicular band centered near 2083 cm^{-1} . Matching those Q -branches is a series of strong P -branch lines that have an effective $A\zeta$ value close to the value found for ν_{22} . Consequently we believe those transitions must belong to the binary band $\nu_4+\nu_{22}$ (E) which is predicted at 2092 cm^{-1} . Since the Gaussian calculations indicate that ν_3 is close to ν_4 , an alternative assignment is that this band is $\nu_3+\nu_{22}$, predicted at 2095 cm^{-1} . However, as seen in Table 5, comparison of the predicted intensities, ΔA , ΔB and $A\zeta$ values definitely favors the

³The experimental wavenumber values assigned for spiropentane by Burns and McGavin [4] suggest other combinations in this region involving ν_3 , ν_8 , and ν_{11} fundamentals. These are not considered here since, as discussed in our earlier paper [6], we believe these to be misassignments since their assigned values differ significantly from the theoretical values, by -119 , -85 , and $+116 \text{ cm}^{-1}$, respectively.

$\nu_4+\nu_{22}$ assignment. Assuming that assignment is correct, it implies that ν_4 is at about 1030 cm^{-1} , close to the 1037 cm^{-1} Raman feature assigned as ν_4 for liquid spiropentane [3].

Since the $\nu_3+\nu_{22}$ and $\nu_4+\nu_{22}$ states are quite close together, there are probably strong interactions between them that would mix the states. This could explain the observation that the *R*-branch transitions are much weaker than the *P*-branch lines so that no transitions involving upper state $kl>0$ levels have been found. In addition there are quite a few other nearby binary vibrational states that could be involved, such as $\nu_{11}+\nu_{22}$ (*E*) near 2064 cm^{-1} , $2\nu_4$ (A_1) near 2067 cm^{-1} , $\nu_3+\nu_4$ (A_1) near 2071 cm^{-1} , $2\nu_3$ (A_1) near 2074 cm^{-1} , $2\nu_{22}$ (A_1 , B_1 , B_2) near 2116 cm^{-1} and $\nu_5+\nu_{21}$ (*E*) near 2120 cm^{-1} . In view of this, speculation on the causes of the missing $\Delta kl = +1$ transitions seems unwarranted at this time. The constants resulting from the least-squares fit for this band are given in Table 2.

3.9 Other fundamental bands observed, but for which the rotational analysis was not attempted or was unsuccessful.

No bands in the CH stretching region were examined since experience has shown these to be usually complex because of mixing with overtone and combination bands that can occur in this region. The spectra should be simpler at the low frequency extreme, where two fundamentals are predicted, ν_{12} (B_1) at 292 cm^{-1} and a perpendicular band, ν_{23} (*E*) at 308 cm^{-1} . Some weak structure was seen near 300 cm^{-1} but we were unsuccessful in assigning it, possibly due to overlapping hot-band contributions and relatively poor signal-to-noise in the spectra.

A parallel band, ν_{17} , and a perpendicular band, ν_{23} , are expected to occur near 880 cm^{-1} and the spectrum does show very strong absorption in this region, with a *Q*-branch at about 871 cm^{-1} . Unfortunately, most of the high resolution spectrum of this region is very cluttered and does not show the type of order that one would expect for a parallel band, nor does it show a pattern that can be identified with assignable transitions for a perpendicular band. Only in a region at about 868 cm^{-1} does a pattern emerge that looks like a *P*-branch for a parallel band, presumably ν_{17} . However, no corresponding *R*-branch transitions could be identified, although there are many transitions in the *R*-branch region (but no apparent order). Since the ν_{23} fundamental is expected to be very close to 870 cm^{-1} one might expect to observe a strong $\Delta k = \pm 1$, $\Delta l = \pm 1$ Coriolis interaction, but efforts to include this in the analysis were not enlightening. We note that two other states are predicted by the Gaussian calculations to occur in the 880 cm^{-1}

region, $\nu_5+\nu_{12}$ (B_1) at 889 cm^{-1} and $\nu_5+\nu_{25}$ (E) at 896 cm^{-1} . Both of these can interact with both ν_{17} and ν_{23} , with dramatic effects on the intensity patterns, so the complexity of the bands is perhaps not surprising.

A similar difficulty occurs for the perpendicular ν_{21} band, which appears as a weak feature at about 1150 cm^{-1} . In addition to ν_{21} , predicted at 1158 cm^{-1} , other states predicted in this region are $\nu_8+\nu_{12}$ (B_2), $\nu_8+\nu_{25}$ (E), $\nu_{12}+\nu_{17}$ (A_2) and $\nu_{12}+\nu_{23}$ (E) at 1132 , 1148 , 1164 and 1173 cm^{-1} , respectively. The spectrum shows a complex mix of lines with no discernable pattern that could aid in making a rotational analysis.

Finally, according to our Gaussian predictions, there should be three fundamental vibrations near 1400 cm^{-1} , ν_2 (A_1), ν_{15} (B_2) and ν_{20} (E), predicted at 1457 , 1402 and 1431 cm^{-1} , respectively. The latter two are both Raman and infrared active and are consistent with the observation in the liquid of strong Raman bands near 1397 and 1427 cm^{-1} . In our infrared spectra we see no sign of a parallel band in this region but we can fit some transitions to a perpendicular pattern for a band which is presumed to be ν_{20} , with a rQ_0 sub-band observed at 1428.15 cm^{-1} . Judging by the quickly-changing shape of the Q -branches, the upper-state for this band must be perturbed by some other nearby state possibly $\nu_5+\nu_8$ (A_2) or $\nu_7+\nu_{12}$ (B_2), predicted at 1426 and 1436 cm^{-1} , respectively. Both could Coriolis-couple with ν_{20} , making a detailed rotational analysis problematic.

4. Discussion

4.1 Comparison of the observed constants with those given by the Gaussian calculation

Table 1 lists the experimental values for the ground state constants and it is considered remarkable that just four parameters suffice to fit more than 5600 level spacings to a standard deviation of only 0.00037 cm^{-1} . (Many of these are of course duplicate combination-differences due to the use of data from several bands.) It is seen that B_0 is within 0.5 % of the theoretical prediction and the two quartic centrifugal constants D_J and D_{JK} differ from theory by only 1.7 and 0.8 %, respectively. This agreement justifies fixing A_0 and D_K constants at the theoretical values in the fitting process since, although the transition frequencies are independent of A_0 and D_K , the calculated line intensities are not.

Good agreement is also seen for the small $K = 2$ splitting constant Δ_2 , which for the ground state can be taken to be very close to the value of d_2 computed for the equilibrium

structure. The quartic distortion constants, including d_2 , depend only on the harmonic potential energy terms and, in the D_{2d} case of spiropentane, theory [16] predicts that $d_2 = (\tau_{xxxx} + \tau_{yyyy} - 2\tau_{xxyy})/64$, where the Wilson-Howard [17] τ constants depend only on the derivatives of the moments of inertia with respect to the normal modes. The Gaussian values are $\tau_{xxxx} = \tau_{yyyy} = -0.871 \times 10^{-7} \text{ cm}^{-1}$ and $\tau_{xxyy} = -1.260 \times 10^{-7} \text{ cm}^{-1}$, giving a positive value of $+1.22 \times 10^{-9}$ for d_2 . This is within 4.1 % of the experimental value which, with our level-ordering convention, is also of positive sign.

For excited vibrational states, theoretical calculations at the anharmonic level yield improved estimates of the vibrational frequencies ν , in most cases within 1%. However larger deviations can occur when Fermi and Coriolis interactions occur between nearby states and more recent versions of the Gaussian programs attempt to account for these. This accounts for some of the variability found in Gaussian anharmonic frequencies when using different versions of the Gaussian program.

Theory also leads to predictions of the changes in the rotational constants $\Delta A = A' - A'' = -\alpha_A$ and $\Delta B = B' - B'' = -\alpha_B$ with vibrational state. The latter constants depend only on the quadratic and cubic terms in the potential and, for a given state, generally have the correct sign and are within about 20% of the experimental values. Such is the case for ν_{24} , where agreement is better than 10% because there are no interactions with nearby states. However poorer agreement occurs for most of the other cases in Table 5 and the agreement of $A\zeta$ values is also generally poorer than normal, due to such interactions.

4.2 The observed splitting constants

As shown in Figure 3, the degenerate states of a molecule with D_{2d} symmetry such as spiropentane have both $kl = -1$ and $kl = +1$ levels split by terms that we have labeled q^- and q^+ . Those same constants also result in a smaller, but observable splitting of the $kl = -3$ and $kl = +3$ levels. In the case of allene the A value is so large that the coupling between the $K = 1$ and $K = 3$ levels is too small to cause a measureable splitting of the $K = 3$ levels. For allene the analysis used intensity arguments to determine which levels are A_1 or A_2 or B_1 or B_2 but for spiropentane the intensity difference is smaller, 76/60 vs 2/1, and there are very many unidentified hot-band and overlapping transitions so the intensity measurements are less reliable.

As mentioned above, the infrared rovibrational selection rules allow $A_1 \leftrightarrow B_1$, $A_2 \leftrightarrow B_2$, and

$E \leftrightarrow E$ transitions only and, as can be seen in Figure 3, the rQ_0 transitions will all involve upper state levels that are different from the levels that are reached by the rR_0 and rP_0 transitions. That provides a method of determining the order of the split B_1 and B_2 levels for both $kl = +1$ and $kl = -3$ without making any intensity measurements. Intensity measurements are needed for the A_1/A_2 splitting and this proved possible for many lines of the ν_{24} band. Consequently we are confident that Figure 3 gives the correct ordering of the A_1 and A_2 levels as well as the B_1 and B_2 levels, both for the upper state, ν_{24} , and for the ground state. The other perpendicular band that was studied, ν_{22} , was found to have the order of the $kl = +1$ B_1 and B_2 levels reversed compared to ν_{24} , as was the case for the $kl = -1$ A_1 and A_2 levels. The experimental results (in cm^{-1}) are ν_{22} : $q^+ = 0.000114$, $q^- = -0.000012$; ν_{24} : $q^+ = -0.000138$, $q^- = 0.000549$.

The q constants and the α 's are of comparable magnitude and both depend upon quadratic and cubic potential terms, with no dependence on quartic terms. Comparisons of experimental q^+ and q^- values with theoretical Gaussian values would be desirable but these values are not computed in the program. In principle one can obtain the signs and magnitudes of these using the theoretical relations of Grenier-Besson [18] and the cubic force constants and other parameters generated by Gaussian. In practice we have found this difficult because of uncertainty regarding the labeling of the symmetries of the components of degenerate vibrations; efforts to resolve this and some other inconsistencies in the Gaussian output are underway.

Acknowledgments

J. Nibler acknowledges a Camille and Henry Dreyfus Senior Scientist Mentor Award which provided support of undergraduates Joseph Price and Jared Harzan. The infrared spectra were recorded at the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated for the United States Department of Energy by the Battelle Memorial Institute under contract DE-AC05-76RLO 1830. We thank Robert Sams of PNNL for helpful advice and assistance in recording the infrared spectra of spiropentane at this facility.

References

1. S. W. Benson, *Thermochemical Kinetics*, 2nd. ed., (1976) p. 273, Wiley, New York.
2. M.J. Murray, E.H. Stevenson, *J. Am. Chem. Soc.* 66 (1944) 812-816.
3. F.F. Cleveland, M.J. Murray, W.S. Gallaway, *J. Chem. Phys.* 15 (1947) 742-758.
4. G.R. Burns and D.G. McGavin, *Appl. Spectrosc.* 26 (1972) 540-542.
5. L.J. Schaad and A.A. Jarzęcki, *J. Mol. Struct. (Theochem)* 341 (1995) 271-278.
6. J.E. Price, K.A. Coulterpark, T. Masiello, J.W. Nibler, A. Weber, A. Maki, T.A. Blake, *J. Mol. Spec.* 269 (2011) 129-136.
7. L.S. Rothman *et al.* HITRAN and *J. Quant. Spectrosc. Radiat. Transfer* 96 (2005) 139-204.
8. A.G.Maki, J.S. Wells, *Wavenumber Calibration Tables from Heterodyne Frequency Measurements*, NIST Specieal Publication 821, US Department of Commerce, 1991. <<http://physics.nist.gov/PhysRefData/wavenum/html/contents.html>> (accessed 1995).
9. G.J. Cartwright and I.M. Mills; *J. Mol. Spec.*, 34 (1970) 415-439.
10. F. Hegelund, N. Andresen and M. Koivusaari. *J. Mol. Spec.*, 149 (1991) 305-313; 159 (1993) 230-248.
11. S. Nissen, F. Hegelund, M. S. Johnson, and B. Nelander, *J. Mol. Spec.*, 216 (2002) 51-61.
12. J.W. Nibler, A. Weber, and A. Maki, A. Weber, J.W. Nibler, T. Masiello, T.A. Blake, R. Kirkpatrick, *J. Mol. Spec.* 264 (2010) 26-36
13. R. Kirkpatrick, T. Masiello, M. Martin, J.W. Nibler, A. Maki, A. Weber, and T.A. Blake, *J. Mol. Spec.* 281 (2012) 51-62.
14. B.N, Taylor, C.E. Kuyatt, NIST Technical Note No. 1297 (1994), *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*. This publication may be downloaded from <http://physics.nist.gov/Pubs/guidelines/contents.html>.
15. A. Perry, M.A. Martin, J.W. Nibler, A.Maki, A. Weber, and T.A. Blake, *J. Mol. Spectrosc.* 22-23 (2012) 22-32.
16. J. K. G. Watson, in *Vibrational Spectra and Structure*, Vol. 6, J. Durig, Ed., Elsevier, Amsterdam, (1997) 1-24.
17. E.B. Wilson Jr. and J.B. Howard. *J. Chem. Phys.*, 4 (1936) p. 260.

18. M.L. Grenier-Besson, J. Phys. Radium, 21 (1960) 555-565.

LIST OF TABLES

Table 1 Rotational parameters (in cm^{-1}) for the ground state of spiropentane.

Table 2. Rovibrational parameters (in cm^{-1}) for ν_{22} , ν_{24} , and $\nu_4+\nu_{22}$ of spiropentane.

Table 3 Rovibrational parameters (in cm^{-1}) for ν_{16} and $2\nu_{22}$ of spiropentane.

Table 4. Rovibrational parameters (in cm^{-1}) for ν_{14} and for either $2\nu_{24}$ or $\nu_5+\nu_{16}$ of spiropentane.

Table 5. Comparison of some experimental and theoretical rovibrational parameters for spiropentane.

LIST OF FIGURES

Figure 1. The observed and calculated spectrum of the ν_{24} perpendicular fundamental band of spiropentane. The assigned P , Q , and R line sequences are shown with dots in the lower trace.

Figure 2. An enlarged view of a segment of ν_{24} showing some of the rQ_2 transitions of spiropentane that are split into $A_1 \leftarrow B_1$ and $A_2 \leftarrow B_2$ transitions with respective relative intensities 76 to 60 as predicted from the nuclear spin weights. Also indicated are rQ_3 and rQ_4 sequences that show no splittings.

Figure 3. Energy level diagram for the ν_{24} (E) state and for the ground state (A_1) of spiropentane. The order of the levels, *i.e.* which levels are above the other levels, is correct, but the scale is not. The number in parentheses gives the nuclear spin weight of the level. Allowed infrared rovibrational transitions are $A_1 \leftarrow B_1$, $A_2 \leftarrow B_2$ and $E \leftarrow E$; a few $\Delta J = 0$, $\Delta K = \pm 1$ Q -branch transitions are shown.

Figure 4. The observed and calculated parallel bands of spiropentane in the 1550 cm^{-1} region. For display purposes, a number of intense water vapor lines have been deleted in the spectrum. The lower wavenumber band is ν_{14} . The calculated upper band is for $\nu_5+\nu_{16}$, but a nearly identical simulation is obtained for $2\nu_{24}$ (B_2), whose assignment is slightly favored (see text).

Figure 1

Figure 2

Figure 3

Figure 4

Table 1
Rotational parameters (in cm^{-1}) for the ground state
of spiropentane

Parameter ^a	Experimental	Theoretical B3LYP/cc-pVTZ
A_0	[0.35059]	0.35059
B_0	0.13947411(15)	0.13877
$D_J \times 10^8$	2.4615(15)	2.420
$D_{JK} \times 10^8$	8.66(4)	8.590
$D_K \times 10^8$	[5.21] ^b	5.21
$H_J \times 10^{13}$	[0.0]	0.053
$H_{JK} \times 10^{13}$	[0.0]	-5.45
$H_{KJ} \times 10^{13}$	[0.0]	8.99
$H_K \times 10^{13}$	[0.0]	-3.90
$\Delta_2 \times 10^9$	1.172(16)	1.22
$J_{max} =$	96	
$K_{max} =$	31	
# differences	5612	
rms dev. (cm^{-1})	0.00037	

^aGiven in parentheses here and in subsequent tables are uncertainties in the last digits (twice the standard deviation = type B, k=2, uncertainties as defined in Ref. [14].)

^bValues given in square brackets were held fixed.

Table 2Rovibrational parameters (in cm^{-1}) for ν_{22} , ν_{24} , and $\nu_4+\nu_{22}$ of spiropentane

Parameter ^a	ν_{22}	ν_{24}	$\nu_4+\nu_{22}$
ν_0	1051.36066(4)	779.12623(3)	2081.52595(19)
$\Delta A \times 10^3$	-0.2534(4)	-0.65283(12)	-0.699(9)
$\Delta B \times 10^3$	-0.08790(6)	-0.28430(6)	-0.14297(24)
$\Delta D_J \times 10^8$	0.3662(22)	-0.2439(33)	0.247(7)
$\Delta D_{JK} \times 10^8$	-2.792(16)	2.300(10)	3.15(32)
$\Delta D_K \times 10^8$	1.28(8)	-2.038(12)	31.1(9)
$\Delta H_J \times 10^{13}$	[0.0] ^b	-0.454(58)	[0.0]
$\Delta H_{JK} \times 10^{13}$	[0.0]	9.92(25)	[0.0]
$\Delta H_{KJ} \times 10^{13}$	[0.0]	-26.2(5)	-102.(26)
$\Delta H_K \times 10^{13}$	[0.0]	17.8(4)	[0.0]
$A\zeta$	-0.0017402(26)	0.0022338(10)	-0.00179(4)
$\eta_J \times 10^5$	0.1129(6)	0.21260(24)	0.0141(52)
$\eta_K \times 10^5$	-0.1329(18)	-0.21500(29)	-1.29(5)
$\eta_{JJ} \times 10^{10}$	-0.085(21)	0.616(11)	[0.0]
$\eta_{JK} \times 10^{10}$	2.49(13)	[0.0] ^c	[0.0]
$\eta_K \times 10^{10}$	[0.0]	-0.564(13)	[0.0]
$q^+ \times 10^3$	0.1138(5)	-0.13780(19)	[0.0]
$q^+_J \times 10^8$	0.559(24)	0.093(8)	[0.0]
$q^+_K \times 10^8$	[0.0]	-17.87(19)	[0.0]
$q^- \times 10^3$	-0.0124(4)	0.54922(12)	-0.0137(4)
$q^-_J \times 10^8$	-2.403(24)	-0.456(5)	[0.0]
$q^-_K \times 10^8$	[0.0]	19.81(11)	[0.0]
$w_{4,0} \times 10^8$	[0.0]	-0.1366(16)	[0.0]
$J_{\max} =$	69	74	55
$K_{\max} =$	24	52	31
# transitions	3370	5709	1143
rms dev. (cm^{-1})	0.00039	0.00027	0.00054

^a $\Delta B = B' - B''$, $\Delta A = A' - A''$, etc.^bValues given in square brackets were held fixed.

Table 3

Rovibrational parameters^a (in cm⁻¹) for ν_{16} and $2\nu_{22}$ of spiropentane

Parameter	ν_{16} (B_2)	$2\nu_{22}$ (B_2)
ν_0	992.53792(3)	2098.21151(15)
$\Delta A \times 10^3$	-1.01921(21)	-0.5860(26)
$\Delta B \times 10^3$	0.024718(25)	-0.14225(20)
$\Delta D_J \times 10^8$	0.0335(6)	0.596(5)
$\Delta D_{JK} \times 10^8$	0.436(8)	-9.78(23)
$\Delta D_K \times 10^8$	-11.73(4)	-14.22(30)
$\Delta H_J \times 10^{13}$	0.022(5)	[0.0] ^b
$\Delta H_{JK} \times 10^{13}$	-0.75(7)	[0.0]
$\Delta H_{KJ} \times 10^{13}$	20.8(6)	[0.0]
$\Delta H_K \times 10^{13}$	-141.1(18)	[0.0]
$\Delta_2 \times 10^9$	-1.108(3)	[0.0]
$A\zeta$		0.000001(10)
$J_{max} =$	103	68
$K_{max} =$	43	29
# transitions	3371	452
rms dev. (cm ⁻¹)	0.00023	0.00042

^a $\Delta B = B' - B''$, $\Delta A = A' - A''$, etc.

^bValues given in square brackets were held fixed.

Table 4Rovibrational parameters (in cm^{-1}) for ν_{14} and for either $2\nu_{24}$ or $\nu_5+\nu_{16}$ of spiropentane

Parameter ^a	$\nu_{14}(B_2)$	$2\nu_{24}(B_2)$	$2\nu_{24}(A_1)$	$\nu_5+\nu_{16}(B_2)$
ν_0	1539.53206(14)	1567.5223(3)	1569.69(13)	1567.5221(3)
$\Delta A \times 10^3$	-0.6110(9)	-1.190(9)	[-1.190]	-1.394(6)
$\Delta B \times 10^3$	-0.45443(12)	-0.8520(13)	[-0.8520]	-0.8500(12)
$\Delta D_J \times 10^8$	[0.0] ^b	8.84(14)	[8.84]	9.02(14)
$\Delta D_{JK} \times 10^8$	0.56(4)	-3.2(12)	[-3.2]	-37.4(12)
$\Delta D_K \times 10^8$	0.62(17)	[0.0]	[0.0]	-17.5(37)
$\Delta H_J \times 10^{13}$	[0.0]	-187.(5)	[-187.]	-184.(5)
$\Delta H_{JK} \times 10^{13}$	[0.0]	[0.0]	[0.0]	-1240.(51)
$\Delta H_{KJ} \times 10^{13}$	[0.0]	[0.0]	[0.0]	-3372.(308)
$\Delta H_K \times 10^{13}$	72.(9)	[0.0]	[0.0]	3069.(752)
$A\zeta$		0.000961(26)		
$\eta_J \times 10^5$		0.210(10)		
$\eta_{JJ} \times 10^9$		-0.901(39)		
$q+ \times 10^4$		$\pm 0.78(7)$		
$J_{\max} =$	56	48		48
$K_{\max} =$	40	17		17
# transitions	453	416		416
rms dev. (cm^{-1})	0.00039	0.00050		0.00055

^a $\Delta B = B' - B''$, $\Delta A = A' - A''$, etc.^bValues given in square brackets were held fixed.

Table 5Comparison of some experimental and theoretical rovibrational parameters (cm^{-1}) for spiropentane

Parameter ^a	Symmetry	ν_0		Anharmonic Intensity, Theory	$\Delta A \times 10^3$		$\Delta B \times 10^3$		$A\zeta$	
		Expt.	Theory ^b		Expt.	Theory	Expt.	Theory	Expt.	Theory
ν_{14}	B_2	1540	<i>1527</i>	0.32	-0.611	-0.424	-0.454	-0.466		
ν_{16}	B_2	993	998	15.27	-1.019	-1.330	0.025	0.014		
ν_{22}	E	1051	<i>1059</i>	2.04	-0.253	-0.233	-0.088	-0.061	-0.0017	-0.0022
ν_{24}	E	779	784	1.43	-0.653	-0.622	-0.284	-0.259	0.0022	0.0029
$2\nu_{22}$	B_2	2098	2113	1.22	-0.586	-0.466	-0.142	-0.122		-0.0022
$2\nu_{24}$ or	B_2	1568	<i>1579</i>	0.02	-1.182	-1.244	-0.853	-0.518	0.0009	0.0029
$\nu_5 + \nu_{16}?$	B_2	1568	<i>1587</i>	0.42	-1.392	-0.871	-0.852	-0.085		
$\nu_4 + \nu_{22}$ or	E	2082	2092	1.33	-0.698	-0.833	-0.143	-0.131	-0.0018	-0.0022
$\nu_3 + \nu_{22}?$	E	2082	2095	0.12	-0.698	-1.879	-0.143	0.0781	-0.0018	-0.0022
$\nu_5 + \nu_{14}$ or	B_2	2146	2120	0.10	<0.	0.345	-0.90	-0.565		
$\nu_7 + \nu_{11}?$	B_2	2146	2149	0.07	<0.	0.763	-0.90	0.063		

^a $\Delta B = B' - B''$, $\Delta A = A' - A''$. For cases with alternative assignments, those in boldface are favored.^bThe theoretical results (B3LYP/cc-pVTZ) were calculated using the Anharm and Vibrot options of Gaussian G03W.E.01 except for the anharmonic ν_0 and intensity values, which were calculated using Gaussian 09W.D.01. Italicized ν_0 values were corrected by Gaussian for Fermi resonances.

ν_{24} rotation-vibration band of spiropentane