# **Pseudorotation of Cyclopentane and Its Deuteriated Derivatives**

# L. E. Bauman<sup>†</sup> and J. Laane\*

Department of Chemistry, Texas A&M University, College Station, Texas 77843 (Received: June 3, 1987; In Final Form: August 20, 1987)

The gas-phase mid-infrared Raman spectra of cyclopentane, cyclopentane-d, cyclopentane- $1,1-d_2$ , cyclopentane- $1,1,2,2,3,3-d_6$ , and cyclopentane- $d_{10}$  have been recorded and analyzed in order to investigate the vibrational potential energy surface associated with the pseudorotational and radial motions. For cyclopentane two separate combination band series involving the pseudorotation and a CH<sub>2</sub> deformation or a CH<sub>2</sub> wag were observed. The spacings in those series were about 5.4 and 4.1 cm<sup>-1</sup>, respectively. Similar series with spacings of about 5.0 and 3.7 cm<sup>-1</sup> were observed for the  $d_1$  species. Cyclopentane  $d_{10}$  shows one combination band series near 1000 cm<sup>-1</sup> with a spacing of 4.0 cm<sup>-1</sup>. In addition to these combination bands, pseudorotational fine structure was observed in the overtone region of the radial band ( $420-560 \text{ cm}^{-1}$  for the different isotopic species). Previously, the absorption in this region had been mistakenly assigned to a vibrational fundamental. The radial band itself was observed for each species in its Raman spectrum. Computational methods for calculating the energy levels for this type of two-dimensional problem have been developed. Reduced mass calculations for each isotopic species have also been carried out. The observed spectra have been analyzed both by using a one-dimensional approximation model and by calculating a two-dimensional potential energy surface. The results demonstrate that the pseudorotation in cyclopentane is relatively unhindered and that the barrier to planarity is about 5.5 kcal/mol (values ranging from 1808 to 2090 cm<sup>-1</sup> were calculated by using different models for the various isotopic species).

## Introduction

The two out-of-plane ring vibrations of saturated five-membered rings, such as cyclopentane, which have a high barrier to planarity are best described as a pseudorotation and a radial vibration. The pseudorotation resembles a wave moving around the ring. The maximum amplitude of puckering moves around the ring so that the molecule rapidly interconverts between different bent and twisted forms without passing through the planar configuration. The radial vibration is a nearly harmonic vibration in which the amount of puckering oscillates about an equilibrium value.

The concept of pseudorotation was first proposed by Kilpatrick, Pitzer, and Spitzer in 1947 in order to explain the unusual thermodynamic properties of cyclopentane.<sup>1</sup> Their calculations showed that the bent and twisted structures very nearly had the same conformational energy and the pseudorotation should be essentially unhindered. If the assumptions of unhindered pseudorotation and an infinite barrier to planarity are made, then the two-dimensional problem separates into two one-dimensional problems. The energy levels then resemble those of a planar rigid rotor for the pseudorotation (hence the name "pseudorotation") and those of a harmonic oscillator for the radial mode. On the basis of their thermodynamic calculations, Kilpatrick, Pitzer, and Spitzer calculated a value of 0.472 Å for the equilibrium outof-plane displacement for cyclopentane.<sup>2</sup> In 1959, Pitzer and Donath performed more detailed calculations on the conformations and strain energy in cyclopentane and substituted cyclopentanes<sup>3</sup> and predicted barriers to pseudorotation for many of the cyclopentane derivatives.

The first spectroscopic evidence of the pseudorotation vibration was found for tetrahydrofuran in 1965.<sup>4</sup> In the original work the observed far-infrared transitions were analyzed in terms of free pseudorotation. Later work showed that there were small twofold and fourfold barriers to pseudorotation.<sup>5-7</sup> The pseudorotation vibration has also been observed and analyzed for 1,3-dioxolane,<sup>7,8</sup> which has nearly free pseudorotation. Some other molecules which have been analyzed and which have barriers to pseudorotation are thiacyclopentane,9 silacyclopentane,10 silacyclopentane- $1, 1-d_2, 11$  selenacyclopentane, 12 1, 1-difluorocyclopentane,<sup>13</sup> cyclopentanone,<sup>14</sup> and germacyclopentane.<sup>15</sup> Reference 16 summarizes the results for these molecules. Two-dimensional analyses have been performed on germacyclopentane,<sup>17</sup> cyclopentanone,<sup>18</sup> and silacyclopentane.<sup>19</sup> The pure pseudorotational spectrum has not been observed for cyclopentane, but, in 1969

Durig and Wertz reported infrared combination bands (obtained under low resolution) of the pseudorotation vibration with a methylene deformation.<sup>20</sup> The combination bands were separated by approximately 5 cm<sup>-1</sup>. These bands were analyzed assuming unhindered pseudorotation with a pseudorotational constant of 2.54 cm<sup>-1</sup>, which gives an equilibrium out-of-plane displacement of 0.479 Å. The radial band is inactive in the vapor-phase infrared spectrum<sup>1</sup> but has been observed at low temperatures for the solid and liquid phases.<sup>21</sup> It also gives rise to a very weak, broad Raman band in the liquid phase at 288 cm<sup>-1</sup>. In 1972, Carreira, Jiang, Person, and Willis observed three Q branches for the radial vibration in the gas phase.<sup>22</sup> Using this data for a two-dimensional analysis they calculated a barrier to planarity of 1824 cm<sup>-1</sup>. This was the first direct spectroscopic measurement of the barrier to planarity of cyclopentane. Their calculations showed a negative deviation of the pseudorotational levels from those predicted one-dimensionally because of the finite barrier to planarity. The

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Present address: Department of Physics, Mississippi State University, MS 39762.



Figure 1. Reaction scheme for the preparation of deuteriated cyclopentane.

negative deviations had been predicted for cyclopentane as well as for tetrahydrofuran and 1,3-dioxolane.<sup>23,24</sup>

Due to the fivefold symmetry of cyclopentane, only ten- and twentyfold barriers to pseudorotation are allowed. In an effort to observe evidence for a barrier to pseudorotation, Chao and Laane examined the combination bands of cyclopentane at a higher resolution<sup>25</sup> and found the combination bands to be split into doublets. These doublets were believed to be due to Coriolis coupling of the molecular rotation with the pseudorotation vibration. No evidence for a barrier to pseudorotation was found, but a small barrier (<25 cm<sup>-1</sup>) could not be ruled out.

This present investigation was undertaken in an effort to better understand the pseudorotation of cyclopentane. In this investigation several deuteriated cyclopentanes were investigated for pseudorotation combination bands and for the radial band. The isotopic species studied were cyclopentane, cyclopentane-d, cyclopentane- $1,1-d_2$ , cyclopentane- $1,1,2,2,3,3-d_6$ , and cyclopentane- $d_{10}$ . The fivefold symmetry is destroyed in the partially deuteriated compounds, so their selection rules are different. Using the data on the deuteriated compounds and the reduced mass calculations carried out in this work, a two-dimensional analysis of the vibrational potential energy surface was performed.

### **Experimental Section**

A. Preparation of Compounds. Cyclopentane-1,1- $d_2$  and cyclopentane-1,1,2,2,3,3- $d_6$  were synthesized from cyclopentanone by the method of Lipnick.<sup>26</sup> The reaction scheme is outlined in Figure 1. Cyclopentane, cyclopentane-d, and cyclopentane- $d_{10}$  were obtained commercially and purified by using gas chromatography.

1. Preparation of Cyclopentane-1,1-d<sub>2</sub>. a. Cyclopentanol-1-d. A 2.15-g sample of lithium aluminum deuteride was added to 150 mL of anhydrous ether in a 500-mL three-neck round bottom flask fitted with a dropping funnel, chilled water condenser, and a dry nitrogen purge. Fifteen grams of cyclopentanone, dried over magnesium sulfate, was added to 75 mL of anhydrous ether and then was added dropwise to the reaction flask. A white precipitate formed upon each addition. The mixture was refluxed overnight, and then the excess reducing agent was destroyed by the dropwise addition of a saturated ammonium chloride solution. The reaction mixture was filtered through a sintered glass funnel through Celite and then dried over magnesium sulfate. Suction filtration and concentration yielded a pale yellow liquid. A vacuum distillation gave 7.75 g (50% yield) of cyclopentanol-1-d boiling between 58.5 and 60.0 °C at 30 Torr. An NMR spectrum of the alcohol showed two singlets at  $\delta = 3.4$  and 1.6 with an integrated ratio of 1:8.

b. 1-Cyclopentanol-1-d Tosylate. A 7.75-g sample of cyclopentanol-1-d was poured into a flask containing 27.0 g of ptoluenesulfonyl chloride in 40 mL of pyridine (dried over 3 A molecular sieve) at 0 °C in an ice bath. The cold mixture was stirred for 30 min and then was placed in a refrigerator at -5 °C for 48 h. The mixture was then poured into a separatory funnel containing crushed ice and concentrated HCl. Ether (200 mL) was added and the deep yellow aqueous layer was removed. The ether layer was washed with 50 mL of 5% HCl and then 50 mL of saturated bicarbonate solution. The ether was removed on a rotary evaporator yielding 25.7 g of a pale yellow oil. The oil was recrystallized in pentane in a dry ice-acetone bath to give 14.9 g of white crystals which melted at room temperature (70% yield).

c. Cyclopentane-1,1- $d_2$ . A mixture of 14.9 g of cyclopentanol-1-d tosylate in 35 mL of dry tetrahydrofuran was added dropwise over 2 h to a three-neck flask containing a suspension of 3.0 g of lithium aluminum deuteride in 70 mL of dry tetrahydrofuran at 66 °C. A crusty yellow precipitate formed. The reaction flask was equipped with a magnetic stirrer, dropping funnel, reflux condenser, and a dry nitrogen purge. Unreacted reducing agent was destroyed with a 3:1 mixture of tetrahydrofuran and water, forming a large amount of white precipitate. The reaction mixture was then poured into a separatory funnel containing 20 mL of 20% sulfuric acid, crushed ice, and 7 mL of octane. Three layers formed and the bottom layer was removed. The upper layers were washed three times with concentrated sulfuric acid (leaving only one layer), and then once with water and once with a saturated sodium bicarbonate solution. The extraction mixture was distilled on a spinning band column yielding 1.4 g of cyclopentane-1,1- $d_2$  at 52 °C (31% yield). The NMR spectrum showed a singlet at  $1.5\delta$ .

2. Preparation of Cyclopentane-1,1,2,2,3,3- $d_6$ . a. Cyclopentanone-2,2,5,5- $d_4$ . A sample of 42.0 g of cyclopentanone was exchanged four times<sup>27</sup> with a solution of 138.2 g of anhydrous potassium carbonate in 200 mL of D<sub>2</sub>O. Each exchange was refluxed for 24 h and each formed a deep yellow solution with a dark film at the interface of the two layers. Approximately one-third of the organic layer was vacuum transferred (13.1 g) to give a clear solution with a lower layer of about 1 mL of D<sub>2</sub>O. An infrared spectrum of the neat liquid showed bands at 2960 (m), 2875 (m), 2215 (w), 2120 (w), and 1740 (s) cm<sup>-1</sup>.

b. 1-Cyclopentanol-1,2,2,5,5- $d_5$ . The reduction of the ketone and the distillation of the alcohol were carried out by using the procedure described for 1-cyclopentanol-1-d. A sample of 13.1 g of cyclopentanone-2,2,5,5- $d_4$  was reduced to give 9.0 g of 1cyclopentanol-1,2,2,3,3- $d_5$  (67% yield) boiling at 63 °C at 30 Torr. The NMR spectrum showed a singlet at 4.4 $\delta$  and a multiplet at 1.5 $\delta$  with a ratio of 1:4.

c. 1-Cyclopentanol-1,2,2,5,5- $d_5$  Tosylate. A sample of 9.0 g of 1-cyclopentanol-1,2,2,5,5- $d_5$  was reacted to give 16.0 g of 1-cyclopentanol-1,1,2,2,5,5- $d_5$  tosylate (66% yield) by using the same procedure as that described for 1-cyclopentanol-1-d tosylate.

d. Cyclopentane-1,1,2,2,3,3-d<sub>6</sub>. Following the procedure used for cyclopentane-1,1-d<sub>2</sub>, 16.0 g of 1-cyclopentanol-1,2,2,5,5-d<sub>5</sub> tosylate was reduced to give about 0.8 g of cyclopentane-1,1,2,2,3,3-d<sub>6</sub> with a tetrahydrofuran impurity. The sample was purified by using gas chromatography to give 0.3 g of cyclopentane-1,1,2,2,3,3-d<sub>6</sub>. The NMR spectrum showed a singlet at  $1.5\delta$ .

B. Characterization of Compounds. The isotopic purity of the two deuteriated cyclopentane molecules was checked by mass spectrometry. Assuming that only  $M - 1^+$ ,  $M^+$ , and  $M + 1^+$  ions are important and the only impurities were D - 1, i.e., cyclopentane-d and cyclopentane- $d_5$ , then the percentages of impurity were only 2.7% for cyclopentane-1,1- $d_2$  and 1.2% for cyclopentane-1,1,2,2,3,3- $d_6$ . The actual mass spectra are presented elsewhere.<sup>28</sup>

C. Spectroscopic Measurements. All infrared spectra were recorded with a Digilab FTS-20 interferometer. For mid-infrared spectra a germanium-coated KBr beamsplitter was used with a Globar source and a TGS detector with a KBr window. In the

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200-700-cm<sup>-1</sup> range, a 3.75-µm thick Mylar beamsplitter was used with the Globar source and a TGS detector with a polyethylene window. Gas-phase spectra were taken by using 10-cm glass cells with KBr windows or in a Wilks multiple-reflection cell with KBr or polyethylene windows. Resolutions of 0.1-0.5 cm<sup>-1</sup> were used for the gas-phase spectra. Solid-phase spectra were taken by depositing sample on a CsI window attached with indium washers to a liquid nitrogen cooled, copper cold finger. A resolution of 1.0 cm<sup>-1</sup> was used for all solid-phase spectra. Liquid-phase spectra were taken with a resolution of 2.0 cm<sup>-1</sup> in a 0.5-mm KBr cavity cell. Raman spectra were recorded on a Cary 82 Raman spectrophotometer with a Coherent Radiation Laboratory Model 53 argon ion laser. The 5145-Å line was used as the exciting line. The power at the sample for most gas-phase samples was approximately 1 W. Liquid spectra were taken through the test tube bottom of the greaseless stopcock container in which the samples were kept. Gas-phase Raman spectra were taken by using Cary multipass optics. The samples were thoroughly degassed and contained in modified Cary gas cells.<sup>29</sup> Solid-phase samples were deposited on a liquid nitrogen cooled, copper cold finger. The samples were annealed by allowing the samples to just "melt" and then quickly cooling the sample.

#### Theory

The theoretical description of pseudorotation has been presented elsewhere;<sup>1,3,5,6</sup> only the essential features will be presented here. If cyclopentane is treated as a planar  $(D_{5h})$  molecule, then its two out-of-plane ring vibrations are degenerate. The out-of-plane displacement of each ring atom can be expressed as

$$z_{k} = (2/5)^{1/2} q \cos \left[ (4\pi/5)(k-1) + \phi \right]$$
(1)

where  $\phi$  is the phase angle for pseudorotation and q represents the motion of the radial vibration perpendicular to the ring. When  $\phi = n/5$  for n = 0, 1, 2, ..., the ring assumes a bent configuration but for  $\phi = (2n + 1)\pi/10$  the molecule takes on a twisted structure. The Schrödinger equation is

$$\frac{-\hbar^2}{2m}\sum_{k=1}^5 \frac{\partial^2 \psi}{\partial z_k^2} + V\psi = E\psi$$
(2)

where *m* is the reduced mass for the motion. The  $z_k$  are expressed by eq 1 except that two rotations and one translation (which can be represented by the  $z_k$ ) must also be considered. This results in an added contribution  $R_1 \cos (2\pi/5)(k-1) + R_2 \sin (2\pi/5)(k-1) + T$ . After separation of variables separate equations in  $\phi$ and *q* may be written

$$\frac{-\hbar^2}{2mq_0^2}\frac{\partial^2\psi(\phi)}{\partial\phi^2} + V(\phi)\ \psi(\phi) = E_{\phi}\psi(\phi) \tag{3}$$

and

$$\frac{-\hbar^2}{2mq}\frac{\partial}{\partial q}\left[q\frac{\partial\psi q}{\partial q}\right] + V_q\psi_q = E_q\psi_q \tag{4}$$

where  $q_0$  is the equilibrium value of q during the pseudorotational vibration. Because of the symmetry of cyclopentane, the only possible potential terms  $V(\phi)$  for the pseudorotation would involve tenth-order or higher terms (cos 10 $\phi$ , cos 20 $\phi$ , etc.). For free pseudorotation  $V(\phi) = 0$  and the solution to eq 3 gives

$$E_{\phi} = l^2 \hbar^2 / 2mq_0^2 = l^2 B_{\phi} \tag{5}$$

where  $B_{\phi}$  is the pseudorotational constant (similar to a rotational constant) and *l* is the pseudorotational quantum number. This is valid only for small values of *q* (as compared to the bond distances) and only if *q* remains near its equilibrium value of *q* for the pseudorotation. Equation 5 was used by Durig and Wertz to explain their combination band data,<sup>20</sup> and they calculated the value of  $B_{\phi}$  as 2.54 cm<sup>-1</sup>. Chao and Laane<sup>25</sup> have considered the



Figure 2. Contour diagram of a potential energy surface representing free pseudorotation. The energies are given in cm<sup>-1</sup> and  $V = 6.1312q^4 - 210.5538q^2$ .

case where  $V(\phi) = (V_{10}/2)(1 - \cos 10\phi)$  in eq 3 and have shown that  $V_{10} < 25$  cm<sup>-1</sup>.

It is more accurate to consider the pseudorotational and radial modes two-dimensionally. Figure 2 shows a representative twodimensional potential energy surface for free pseudorotation. Any perpendicular slice through the surface will yield the double minimum potential for the radial vibration. The radial motion itself is represented by a motion perpendicular to the minimum (along q) at any of the infinite values of  $\phi$ . During the pseudorotation the molecule follows the circular minimum of the surface as it interconverts between bent and twisted structures. For the figure it is assumed that  $V_{10} = 0$  but it is likely that very small (a few cm<sup>-1</sup>) tenfold barriers actually exist along the surface, representing minor differences in energy for the bent and twist structures. Since  $V_{10}$  has been shown to be small,<sup>25</sup> its effect will be assumed to be negligible in the calculations. Even with  $V_{10}$ = 0, however, the pseudorotational levels will not be quadratically spaced, as in eq 5, due to the effect of the finite barrier to planarity. Also the radial vibration will show a negative anharmonicity because of the double minimum form of the potential.

Ikeda and co-workers<sup>23</sup> have derived the approximate equations for the pseudorotational and radial energy levels, including the effect of the barrier to planarity

$$E_{l} = A_{q}(\beta_{r}l^{2} - D_{r}l^{4})$$
 (6)

$$E_r = A_q [2(2B_q)^{1/2}(r + \frac{1}{2}) - (3r^2 + 3r + 1)/B_q]$$
(7)

where the potential constants  $A_q$  and  $B_q$  (in reduced form) come from

$$V(q) = A_q(q^4 - B_q q^2)$$
(8)

where the new (unscaled) pseudorotational constant is

$$\beta_r = (2/B_q) [1 + 6 \cdot 2^{1/2} B_q^{-3/2} (r + \frac{1}{2})]$$
(9)

where the pseudocentrifugal distortion constant is

$$D_r = 4/B_q^4 \tag{10}$$

and where *l* and *r* are the pseudorotational and radial quantum numbers, respectively. The barrier to planarity is  $A_q B_q^2/4$  and the spacing between the radial transitions is  $\Delta v_r = 6A_q/B_q$ .

While eq 6-10 can serve as a useful approximation, it is more accurate to determine the eigenvalues of the two-dimensional Hamiltonian equation by matrix diagonalization. This procedure will be described in the following section.

## **Calculation of Energy Levels**

A computer program for calculating the energy levels of a two-dimensional potential energy surface, based on isotropic harmonic oscillator wave functions, was written in order to analyze the out-of-plane ring vibrations of cyclopentane. The program was written as described by Carreira, Mills, and Person<sup>30</sup> with

<sup>(29)</sup> Lewis, J. D.; Laane, J.; Malloy, Jr., T. B. J. Chem. Phys. 1974, 61, 2342.

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the exception that the Wang transformation<sup>31</sup> was used to split the Hamiltonian matrix into four symmetry blocks instead of two. The use of this transformation was suggested by Harris et al. for molecules of  $C_{2\nu}$  symmetry.<sup>32</sup> The Hamiltonian used is the simplest two-dimensional Hamiltonian with  $C_{2v}$  symmetry, which in Cartesian coordinates is

$$H = (-\hbar^2/2m_1)(d^2/dx_1^2) - (\hbar^2/2m_2)(d^2/dx_2^2) + A_1x_1^4 + A_2x_2^4 + B_1x_1^2 + B_2x_2^2 + C_{12}x_1^2x_2^2$$
(11)

where  $m_1$  and  $m_2$  are the respective reduced masses for the  $x_1$  and  $x_2$  vibrational coordinates. The units of the potential energy parameters  $A_1$ ,  $A_2$ , and  $C_{12}$  are cm<sup>-1</sup>/Å<sup>4</sup> and the units of  $B_1$  and  $B_2$  are cm<sup>-1</sup>/Å<sup>2</sup>.

To remove the reduced mass from the expression, mass-weighted coordinates,  $Q_1 = m_1^{1/2} x_1$  and  $Q_2 = m_2^{1/2} x_2$ , are used and the Hamiltonian is then

$$H = (-\hbar^2/2)(d^2/dQ_1^2) - (\hbar^2/2)(d^2/dQ_2^2) + (A_1/m_1^2)Q_1^4 + (A_2/m_2^2)Q_2^4 + (B_1/m_1)Q_1^2 + (B_2/m_2)Q_2^2 + (C_{12}/m_1m_2)Q_1^2Q_2^2$$
(12)

Transforming to dimensionless coordinates using  $q_1 = \gamma_1^{1/2} Q_1$  and  $q_2 = \gamma_1^{1/2} Q_2$  gives

$$H = (-\hbar^2/2)\gamma_1(d^2/dq_1^2) - (\hbar^2/2)\gamma_2(d^2/dq_2^2) + (A_1/m_1^2\gamma_1^2)q_1^4 + (A_2/m_2^2\gamma_2^2)q_2^4 + (B_1/m_1\gamma_1)q_1^2 + (B_2/m_2\gamma_2)q_2^2 + (C_{12}/m_1m_2\gamma_1\gamma_2)q_1^2q_2^2$$
(13)

The transformation coefficients,  $\gamma_1$  and  $\gamma_2$ , are important in making the most efficient use of the basis functions, and are calculated by

$$\gamma_i = (2v_{\max} + 1) / (m_i(x_i)^2)$$
(14)

where  $v_{max}$  is the maximum quantum number used,  $m_i$  is the reduced mass for coordinate i and  $x_i$  is the value of the vibrational coordinate at twice the energy for which accurate eigenvalues are desired. The units of  $\gamma_i$  are amu<sup>-1</sup> A<sup>-2</sup>. Transformation to polar coordinates using  $q_1 = q \cos \theta$  and  $q_2 = q \sin \theta$  gives

$$q_1^4 = (3/8)q^4 + (1/2)q^4 \cos 2\theta + (1/8)q^4 \cos 4\theta \quad (15)$$

$$q_2^4 = (3/8)q^4 - (1/2)q^2\cos 2\theta + (1/8)q^4\cos 4\theta \quad (16)$$

$$q_1^2 = (1/2)q^2 + (1/2)q^2\cos 2\theta \tag{17}$$

$$q_2^2 = (1/2)q^2 - (1/2)q^2 \cos 2\theta \tag{18}$$

$$q_1^2 q_2^2 = (1/8)q^4 - (1/8)q^4 \cos 4\theta \tag{19}$$

$$p_1^2 + p_2^2 = p^2 \tag{20}$$

$$p_1^2 + p_2^2 = p^2 \cos 2\theta \tag{21}$$

where the kinetic energy operators are abbreviated as

$$p_i^2 = (-\hbar^2/2)(d^2/dq_i^2)$$
(22)

The Hamiltonian is now

$$H = F_p^2 + G_p^2 \cos 2\theta + A_q^4 + B_q^2 + C_q^2 \cos 2\theta + D_q^4 \cos 2\theta + E_q^4 \cos 4\theta$$
(23)

where

$$F = (\hbar^2 N_a \, 10^{16} / hc)(1/4)(\gamma_1 + \gamma_2) = 33.715(1/4)(\gamma_1 + \gamma_2) \qquad (N_a = \text{Avogadro's no.}) (24)$$

$$G = 33.715(1/4)(\gamma_1 + \gamma_2) \tag{25}$$

$$A = (1/8)(3A_1/m_1^2\gamma_1^2 + 3A_2/m_2^2\gamma_2^2 + C_{12}/m_1m_2\gamma_1\gamma_2)$$
(26)

(30) Carreira, L. A.; Mills, I. M.; Pearson, W. B. J. Chem. Phys. 1972, 56, 1444.

(31) Wang, S. C. Phys. Rev. 1929, 34, 243.

(32) Harris, D. O.; Engerholm, G. G.; Tolman, C. A.; Luntz, A. C.; Keller,
 R. A.; Kim, H.; Gwinn, W. D. J. Chem. Phys. 1969, 50, 2438.

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$$B = (1/2)(B_1/m_1\gamma_1 + B_2/m_2\gamma_2)$$
(27)

$$C = (1/2)(B_1/m_1\gamma_1 - B_2/m_2\gamma_2)$$
(28)

$$D = (1/2)(A_1/m_1^2\gamma_1^2 - A_2/m_2^2\gamma_2^2)$$
(29)

$$E = (1/8)(A_1/m_1^2\gamma_1^2 + A_2/m_2^2\gamma_2^2 - C_{12}/m_1m_2\gamma_1\gamma_2) \quad (30)$$

The units of F, G, A, B, C, D, and E are  $cm^{-1}$ . The computer program was written so that the potential constants could be entered in either dimensioned Cartesian form (with reduced masses and transformation coefficients) or in dimensionless polar coordinate form.

The basis functions used for this program are the two-dimensional isotropic harmonic oscillator wave functions.<sup>24</sup> These are especially well suited for the cyclopentane problem as they are products of rigid rotor and harmonic oscillator functions

$$\phi_{v,l} = N_{v|l|} e^{il\theta} e^{-q^2/2} F_{v|l|}(q) \qquad v = n_1 + n_2; l = \pm v, \pm (v-2), ..., \pm 1 \text{ or } 0 (31)$$

where  $n_1$  and  $n_2$  are the number of functions in the  $q_1$  and  $q_2$ coordinates.  $N_{v|l|}$  is a normalization factor and  $F_{v|l|}(q)$  is the associated Laguerre polynomial which is a polynomial in q with powers of v to |l|

$$N_{v|l|} = [2w!/(w+1)!](2\pi)^{-1/2}; \qquad w = (1/2)(v-|l|)$$
(32)

$$F_{v|l|}(q) = q^{|l|} L_{w+|l|}^{|l|}(q^2)$$
(33)

where  $L_{w+|l|}^{|l|}(q^2)$  is a generating function defined by

$$L_r^s(p) = (d^s/dp^s) [(e^p d^r/dp^r)(p^r e^{-p})]$$
(34)

As an example, the basis function for v = 3 and  $l = 1, |3,1\rangle$ , is found as follows:

$$w = (v - |l|)/2 = 1$$
,  $s = |l| = 1$ ,  $r = w + l = 2$  (35)

$$F_{3,1}(q) = qL_2^1(q^2) = -4q + 2q^3$$
(36)

$$N_{3,1} = [(2(1!))/2!](2\pi)^{-1/2} = (2\pi)^{-1/2}$$
(37)

$$|3,1\rangle = (2/\pi)^{1/2}(-2q + q^3)e^{-q^2/2}e^{i\theta}$$
(38)

The Hamiltonian matrix elements are integrals of the basis functions over the Hamiltonian operators

$$\langle v', l| H| v, l \rangle = \int_{\theta=0}^{2\pi} \int_{q=0}^{\infty} \phi_{v', l'}^* H \phi_{v, l} q \, \mathrm{d}q \, \mathrm{d}\theta \tag{39}$$

Finding the matrix elements by integration would be a lengthy process, so instead the following shift operators were used

$$F^{++} = (q_1 + iq_2) - i(p_1 + ip_2)$$
(40)

$$F^{+-} = (q_1 - iq_2) - i(p_1 - ip_2)$$
(41)

$$F^{-+} = (q_1 + iq_2) + i(p_1 + ip_2) \tag{42}$$

$$F^{--} = (q_1 - iq_2) + i(p_1 - ip_2)$$
(43)

where

$$F^{++}|v,l\rangle = -(2(v+l+2))^{1/2}|v+1,l+1\rangle$$
(44)

$$F^{+-}|v,l\rangle = (2(v-l+2))^{1/2}|v+1,l-1\rangle$$
(45)

$$F^{-+}|v,l\rangle = (2(v-l))^{1/2}|v-1,l+1\rangle$$
(46)

$$F^{-}|v,l\rangle = -(2(v+l))^{1/2}|v-1,l-1\rangle$$
(47)

Each term in the Hamiltonian can be expressed as a combination of shift operators and the matrix elements found by their application

$$p^{2} = p_{1}^{2} + p_{2}^{2} = -(1/4)(F^{++} - F^{++})(F^{--} - F^{+-})$$
(48)

$$p^{2} \cos 2\theta = p_{1}^{2} - p_{2}^{2} = (-1/16)((F^{-+} - F^{++} + F^{--} - F^{+-})^{2} + (F^{-+} - F^{++} - F^{--} + F^{+-})^{2})$$
(49)

$$q^{4} = (q_{1}^{2} + q_{2}^{2})^{2} = (1/16)(F^{++} + F^{-+})^{2}(F^{+-} + F^{--})^{2}$$
(50)

$$q^{2} = q_{1}^{2} + q_{2}^{2} = (1/4)(F^{++} + F^{-+})(F^{+-} + F^{--})$$
(51)  
$$q^{2} \cos 2\theta = q_{1}^{2} - q_{2}^{2} = (1/8)((F^{++} + F^{-+})^{2} + (F^{+-} + F^{--})^{2})$$
(52)

$$q^{4} \cos 2\theta = (q_{1}^{2} + q_{2}^{2})(q_{1}^{2} - q_{2}^{2})$$

$$= (1/32)(F^{++} + F^{-+})(F^{+-} + F^{--}) \times (F^{++} + F^{-+})^{2} + (F^{+-} + F^{--})^{2}) (53)$$

$$q^{4} \cos 4\theta = 2(q_{1}^{2} - q_{2}^{2})^{2} + (q_{1}^{2} + q_{2}^{2})$$

$$= (1/32)((F^{++} + F^{-+})^{2} + (F^{+-} + F^{--})^{2})^{2} - (1/16)(F^{++} + F^{-+})^{2}(F^{+-} + F^{--})^{2} (54)$$

As an example, the matrix elements for the  $q^2$  operator were found as follows

$$q^{2}|v,l\rangle = \frac{1}{4}(F^{++} + F^{-+})(F^{+-} + F^{--})|v,l\rangle$$

$$= -\frac{1}{4}(2(v-l+2))^{1/2}(2(v+l+2))^{1/2}|v+2,l\rangle + \frac{1}{4}(2(v+l))^{1/2}(2(v+l))^{1/2}|v,l\rangle + \frac{1}{4}(2(v-l+2))^{1/2}(v-l+2))^{1/2}|v,l\rangle - \frac{1}{4}(2(v+l))^{1/2}(2(v-l))^{1/2}|v-2,l\rangle$$
(55)

$$v+2, l|q^2|v, l\rangle = -(1/2)(v-l+2)^{1/2}(v+l+2)^{1/2}$$
 (56)

$$\langle v, l | q^2 | v, l \rangle = (v + l)$$
 (57)

$$\langle v-2, l|q^2|v, l\rangle = -(1/2)(v+l)^{1/2}(v-l)^{1/2}$$
 (58)

The matrix elements are listed in Table I. The  $q^4$  and  $q^2$  elements were checked against those found by Shaffer;<sup>34</sup> however, a few sign errors in the  $q^4$  elements have been pointed out by Bell.<sup>33</sup>

The application of the Wang transformation takes the basis functions from  $e^{il\theta}$  to  $\cos l\theta$  and  $\sin l\theta$  functions. To begin with, the Hamiltonian matrix is split into even an odd blocks due to the fact that only even powers of  $x_1$  and  $x_2$  are included in the Hamiltonian. The Wang transformation splits the Hamiltonian matrix into four blocks-even cosine, even sine, odd cosine, and odd sine blocks. The new Hamiltonian matrix can be found by matrix multiplication,  $\mathbf{H}' = \mathbf{T}^{t} H \mathbf{T}$ , where **T** is the transformation matrix, t denotes transpose and H' is the new Hamiltonian matrix. Figure 3 shows the transformation matrix for the even block and maximum v,  $v_{max}$ , of 6. The matrix would be the same for the odd block, excluding the l = 0 elements. When setting up the Hamiltonian matrix in the four symmetry blocks, the Wang transformation has the following effects on the matrix elements as listed in Table I.

1.  $p^2$ ,  $q^2$ , and  $q^4$  terms are diagonal in l and are unchanged. 2.  $\cos 2\theta$  terms

a. Multiply matrix terms by  $2^{1/2}$  for l = 0.

b. In the odd blocks, the  $l = \pm 1$  terms become diagonal in l for l = +1 and for l = -1 the signs are reversed.

3.  $q^4 \cos 4\theta$  terms

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a. Multiply matrix terms by  $2^{1/2}$  for l = 0.

b. In the even blocks,  $l = \pm 2$  terms become diagonal in l for l = 2 and for l = -2 the signs are reversed.

c. In the odd blocks,  $l = \pm 1$  and  $l' = \pm 3$  terms become l'=  $l \pm 2$  terms for  $l = \pm 1$  and  $l = \pm 3$  (multiplied by -1 for the -l terms).

Figure 4 illustrates the effect of the Wang transformation on the even block.

In the computer program the first matrix blocks are set up, changed to tridiagonal form, and then solved for the eigenvalues and eigenvectors, using the Givens-Householder matrix diagonalization procedure. The first 15 eigenvalues and eigenvectors were calculated for each of the four blocks and then ordered. The least-squares adjustment was included based on that written by Ueda and Shimanouchi.<sup>35</sup> The change in each force constant,  $\Delta F$ , is given by

$$\Delta F = (\mathbf{J}^{\mathsf{t}} \mathbf{W} \mathbf{J})^{-1} (\mathbf{J}^{\mathsf{t}} \mathbf{W} \Delta \nu)$$
(59)

(33) Bell, S. J. Phys. B 1970, 3, 745.

- (34) Shaffer, W. H. Rev. Mod. Phys. 1944, 16, 245.
- (35) Ueda, T.; Shimanouchi, T. J. Chem. Phys. 1967, 47, 4042.

**TABLE I: Matrix Elements** 

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D

q

operator				
(op)	v'	l'	$\langle v', l'   op   v, l \rangle$	
$p^2$	v + 2	1	$\frac{1}{2}((v-l+2)(v+l+2))^{1/2}$	
•	v	1	(v + 1)	
	v – 2	l	$\frac{1}{2}((v-l)(v+l))^{1/2}$	
$p^2 \cos 2\theta$	v + 2	<i>l</i> ± 2	$-\frac{1}{4}((v \pm l + 2)(v \pm l + 4))^{1/2}$	
	v	<i>l</i> ± 2	$-\frac{1}{4}((v \ \theta \ l)(v \pm l + 2))^{1/2}$	
	v – 2	<i>l</i> ± 2	$-\frac{1}{4}((v+l)(v \neq l-2))^{1/2}$	
$q^4$	v + 4	I	$\frac{1}{4}((v+l+2)(v+l+4)(v-l+2)(v-l+4))^{1/2}$	
	v + 2	1	$-(v + 2)((v + l + 2)(v - l + 2))^{1/2}$	
	v	1	$\frac{1}{2}(3v^2 - l^2 + 6v + 4)$	
	v - 2	1	$-(v)((v + l)(v - l))^{1/2}$	
•	v-4	l	$\frac{1}{4}((v+l)(v+l-2)(v-l)(v-l-2))^{1/2}$	
$q^2$	v + 2	l	$-\frac{1}{2}((v+l+2)(v-l+2))^{1/2}$	
	v	1	(v+1)	
2	v-2	1	$\frac{-1}{2}((v+l)(v-l))^{1/2}$	
$q^2 \cos 2\theta$	v + 2	$1 \pm 2$	$1/4((v \pm l + 2)(v \pm l + 4))^{1/2}$	
	v	$l \pm 2$	$-\frac{1}{2}((v \pm l)(v \pm l - 2))^{1/2}$	
4	v-2	$1 \pm 2$	$\frac{1}{4}((v+1)(v+1-2))^{1/2}$	
q <sup>+</sup> cos 20	v + 4	$l \pm 2$	$\frac{-1}{8}((v \pm l + 2)(v \pm l + 4)(v \pm l + 6)(v \pm l + 6)$	Ξ
	v + 2	$l \pm 2$	$\frac{1}{4}(2v p l + 3)((v \pm l + 2)(v \pm l + 4))^{1/2}$	
	v	$l \pm 2$	$-\frac{3}{4}(v+1)((v\pm l)(v\pm l+2))^{1/2}$	
	<i>v</i> - 2	$l \pm 2$	$\frac{1}{4}(2v \pm l + 1)((v + l - 2)(v + l))^{1/2}$	•
4 40	v-4	$l \pm 2$	$\frac{-1}{8}((v+l)(v+l-2)(v+l-4)(v\pm l))^{1/2}$	4
$q^* \cos 4\theta$	v + 4	$l \pm 4$	$\frac{1}{8}((v \pm l + 2)(v \pm l + 4)(v \pm l + 6)(v \pm l + 6)($	l
			$+ 8))^{4/4}$	
	v + 2	$l \pm 4$	$-\frac{1}{2}((v+1)(v \pm 1+2)(v \pm 1+4)(v \pm $	
	v	$l \pm 4$	$\frac{3}{4}((v+l)(v+l-2)(v\pm l+2)(v\pm l+4))^{1/2}$	
	<i>v</i> – 2	<i>l</i> ± 4	$-\frac{1}{2}((v+l)(v+l-2)(v+l-4)(v\pm l+1)(v\pm l+1))(v\pm l+1)(v\pm l+1$	
			$(2))^{1/2}$	
	<i>v</i> – 4	<i>l</i> ± 4	$\frac{1}{8}((v \neq l)(v + l - 2)(v \neq l - 4)(v + l - 6))^{1/2}$	
	1 <sub>6</sub> /	1 2	0 -2 -4-6	
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Figure 3. Wang transformation matrix for the even block of the Hamiltonian matrix with  $v_{max}$  of 6. All elements not shown are zero.

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Figure 4. The effect of the Wang transformation on the even block of the Hamiltonian matrix with  $v_{max} = 6$ .

where  $\Delta v$  is a diagonal matrix of the differences between observed and calculated frequencies, W is a diagonal matrix of weighting factors which are input to the program, J is the Jacobian matrix, and t denotes transpose. The elements of the Jacobian matrix are found as follows

Pseudorotation of Cyclopentane

$$J_{ij} = \mathrm{d}\nu_i/\mathrm{d}F_j = \mathrm{d}V_{nm}/\mathrm{d}F_j \tag{60}$$

where  $\nu_i$  is the *n*-to-*m* calculated transition,  $F_j$  is the force constant being adjusted,  $dV_{nm}/dF_j$  is the difference between expectation values of the operator corresponding to the  $F_j$  potential constants for the *n* and *m* eigenvectors. This is given by

$$dV_{nm}/dF_j = \langle L^t m | \mathbf{V}(j) | L_m \rangle - \langle L^t_n | \mathbf{V}(j) | L_n \rangle$$
(61)

where  $L_m$  is the *m*th eigenvector and V(j) is the matrix representation of the *j*th operator. In calculating the J matrix, the eigenvectors and V(j) matrices must come from the appropriate symmetry blocks.

The program was written so that up to five isotopes could be used in the least-squares adjustment by averaging the  $\Delta F$ 's for each molecule. Damping factors for each isotope were included so that different weights could be given to each isotope.

A subroutine was also included to calculate intensities for transitions for which the dipole operator is  $q_1 = q \cos \theta$  or  $q_2 = q \sin \theta$ . The matrix elements were found by using

$$q \cos \theta = (1/4)(F^{++} + F^{-+} + F^{+-} + F^{--})$$
(62)

$$(q \sin \theta) = (1/4)(F^{++} + F^{-+} - F^{+-} - F^{--})$$

and the elements are

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$$\langle v \pm 1, l \pm 1 | q \cos \theta | v, l \rangle = -(1/4)(2(v \pm l \pm 2))^{1/2}$$
 (63)

$$v \pm 1, l + 1 |q \sin \theta |v, l\rangle = -(1/4)(2(v + l + 2))^{1/2}$$

$$\langle v \pm 1, l - 1 | q \cos \theta | v, l \rangle = + (1/4)(2(v+l))^{1/2}$$
 (64)

 $\langle v \pm 1, l - 1 | q \sin \theta | v, l \rangle = -(1/4)(2(v + l))^{1/2}$ 

The calculated intensities are then found by

$$I \propto \nu_{nm} e^{-(\nu_{nm})/kT} \langle n|q \cos \theta |m\rangle^2$$
 (65)

$$I \propto v_{nm} e^{-(v_{nm})/kT} \langle n|q \sin \theta | m \rangle^2$$

where  $\nu_{nm}$  is the calculated frequency of the *n*-to-*m* transition, the exponential term is due to the Boltzmann factors, and the integral is the transition moment integral found by matrix multiplication. The intensities are normalized so that the most intense transition has a value of 1.0.

The calculated eigenvalues were checked by comparing to previous calculations on 2,5-dihydrofuran<sup>30</sup> and germacyclopentane.<sup>17</sup> The intensities were checked by comparison to those calculated for 2,5-dihydrofuran.

The computer calculations were done on a CDC-1604A computer with a memory of only 32K words. The words are 48 bits, so single precision arithmetic was adequate. The use of the Wang transformation reduces the memory required, so the  $v_{max}$  of 26 could be used.<sup>36</sup> This corresponds to matrices of 105 × 105, 91 × 91, 91 × 91, and 91 × 91. Without the transformation, the largest  $v_{max}$  would be 18. The program as written by Carreira, Mills, and Person<sup>30</sup> had a  $v_{max}$  of 20. For the same  $v_{max}$ , this program is much faster due to the smaller matrix sizes in the diagonalization routine. The larger allowable quantum number is very important in calculating higher energy levels accurately. This was especially important for the calculations on cyclopentane. More recently, we have checked these calculations on a VAX 11/780 computer.

## Results

A. Pseudorotational Combination Bands. The infrared spectrum of cyclopentane was reexamined at a resolution of 0.1  $cm^{-1}$ . In addition to the main combination band series centered at 1460 cm<sup>-1</sup>, a less intense series was observed near 1250 cm<sup>-1</sup>.



Figure 5. Infrared pseudorotational combination bands of cyclopentane. Resolution =  $0.25 \text{ cm}^{-1}$ ; path length = 10 cm; vapor pressure = 52 Torr; no. of scans = 1024.

Figure 5 shows both of these series. The second of these has an average spacing of  $4.1 \text{ cm}^{-1}$ . The bands were observed at 1251.6, 1255.3, 1259.8, 1263.9, 1268.1, and 1272.1 cm<sup>-1</sup>. Figure 6 shows the complicated series of pseudorotational combination bands with a methylene deformation. All of the bands are split into doublets, many into triplets. The doublet splittings are about 1 cm<sup>-1</sup>, ranging from 0.5 to 1.5 cm<sup>-1</sup>.

Two combination bands series were also observed for cyclopentane-*d*, near 1400 cm<sup>-1</sup> and near 1300 cm<sup>-1</sup>, both very weak. Figure 7 illustrates these series of bands. Only difference bands were observed in combination with the methylene deformation with an average spacing of  $5.0 \text{ cm}^{-1}$ . Figure 8 shows these bands. The second series has an average spacing of  $3.7 \text{ cm}^{-1}$ , with bands at 1315.8, 1313.0, 1307.5, 1303.3, and 1301.0 cm<sup>-1</sup>. Zhizhin, Durig, Kasper, and Vasina<sup>37</sup> have previously reported pseudorotational combination bands with a methylene deformation for the  $d_1$ . However, their sample had an impurity of 20% cyclopentane and their combination bands appear to be due to the cyclopentane impurity which has a more intense spectrum.

Pseudorotational combination bands for cyclopentane- $d_{10}$  were observed at approximately 1000 cm<sup>-1</sup> (Figure 9). A difference band series was observed and there also appear to be sum bands, but the series is obscured by other peaks. Figure 10 shows the difference bands that were observed. The average spacing of the bands is 4.0 cm<sup>-1</sup>.

At longer path lengths, the band at 546 cm<sup>-1</sup> of cyclopentane shows pseudorotational fine structure (Figure 11). The analogous band for the  $d_1$  (Figure 12) and  $d_2$  (Figure 13) molecules also show considerable structure. Not enough sample was available to obtain a good spectrum of the  $d_6$  molecule in this region. However, a broad band was observed at 455 cm<sup>-1</sup>. The infrared solid-phase spectrum of the  $d_6$  shows sharp bands at 493, 462, 468, and 445 cm<sup>-1</sup>. The analogous band in the  $d_{10}$  molecule is at 427 cm<sup>-1</sup> and is shown in Figure 14. The broad band at ~490 cm<sup>-1</sup> shows fine structure at long path length. In crystal phase III of cyclopentane the pseudorotation is frozen out<sup>38</sup> and in the solid-phase infrared spectra bands were observed at 547 and 428 cm<sup>-1</sup> for the  $d_0$  and  $d_{10}$  molecules, and doublets were centered at 529, 522, and 464 cm<sup>-1</sup> for the  $d_1$ ,  $d_2$ , and  $d_6$  molecules.

**B.** Radial Bands. The infrared spectrum was searched in the region of the radial band for all five samples and nothing was observed. However, the radial band was observed in the Raman spectrum of each compound. These were very weak bands and the spectra were taken under optimum conditions at the instrumental limit of detection. The spectrum of the  $d_0$  was very similar to that observed by Carreira and co-workers.<sup>22</sup> The Q branches were observed at Raman shifts of 272.5, 264.5, and 257.0 cm<sup>-1</sup>.

<sup>(36)</sup> A much higher  $v_{max}$  can, of course, be attained on a larger computer such as our Amdahl 470 V/6 but there are major cost and convenience advantages to using a small computer.

<sup>(37)</sup> Zhizhin, G. N.; Durig, J. R.; Kasper, J. M.; Vasina, T. V. Zh. Strukt. Khim. 1975, 16, 56.

<sup>(38)</sup> Mills, I. M. Mol. Phys. 1970, 20, 127.



Figure 6. Infrared pseudorotational combination bands of cyclopentane combined with  $E_2'$  methylene deformation. Top spectrum for 52 Torr; bottom spectrum for 311 Torr. Other parameters are the same as for Figure 5.



Figure 7. Infrared pseudorotational combination bands of cyclopentane-d. Resolution  $0.25 \text{ cm}^{-1}$ ; path length = 10 cm; vapor pressure 280 Torr; no. of scans = 512.



Figure 8. Infrared pseudorotational combination bands of cyclopentane-d (expanded spectrum of Figure 7).

Only one Q branch was observed for the  $d_1$  at 268.0 cm<sup>-1</sup>. The recorded Raman spectrum of  $d_2$  is shown in Figure 15. Three Q branches were observed at 261.0, 252.0, and 244.0 cm<sup>-1</sup> (broad). The  $d_6$  molecule showed two Q branches at 240.0 and 228.0 cm<sup>-1</sup> while only one Q branch, at 216 cm<sup>-1</sup>, was observed for the  $d_{10}$  molecule.

C. Calculations of Reduced Masses. It is necessary to calculate reduced masses for the out-of-plane ring vibrations in order to relate the calculated potential functions to actual conformations of the molecule. The model used to calculate the reduced masses is given by eq 1, where the only motion of the carbon atoms is perpendicular to the ring, i.e., in the z coordinate. This assumption



Figure 9. Infrared pseudorotational combination bands of cyclopentane- $d_{10}$ . Resolution = 0.25 cm<sup>-1</sup>; path length = 0.75 m; vapor pressure = 10 Torr; no. of scans = 1024.



Figure 10. Infrared spectrum of the combination bands of cyclopentane- $d_{10}$  (expanded spectrum of Figure 9).

TABLE II: Calculated Reduced Masses for Cyclopentane, Cyclopentane-d, -1,1- $d_2$ , -1,1,2,2,3,3- $d_6$ , and - $d_{10}$ 

phase angle	reduced masses, amu					
$\phi$ , deg	$d_0$	$d_1$	<i>d</i> <sub>2</sub>	<i>d</i> <sub>6</sub>	<i>d</i> <sub>10</sub>	
0	29.00	32.11	34.91	44.20	45.99	
18	29.00	31.82	34.36	43.14	45.99	
36	29.00	31.06	32.92	40.38	45.99	
54	29.00	30.12	31.14	36.96	45.99	
72	29.00	29.36	29.70	34.20	45.99	
90	29.00	29.07	29.14	33.14	45.99	

of the rectilinear motion yields exactly the same reduced mass value for the planar ring as does the use of curvilinear coordinates.



Figure 11. Infrared spectrum of cyclopentane in the radial overtone region. Resolution =  $0.25 \text{ cm}^{-1}$ ; path length = 5.25 m; vapor pressure = 20 Torr; no. of scans = 512.



Figure 12. Infrared spectrum of cyclopentane-*d* in the radial overtone region. Resolution =  $0.25 \text{ cm}^{-1}$ ; path length = 3.75 m; vapor pressure = 20 Torr; no. of scans = 1024.



Figure 13. Infrared spectrum of cyclopentane- $1,1-d_2$  in the radial overtone region. Resolution =  $0.5 \text{ cm}^{-1}$ ; path length = 0.75 m; vapor pressure = 20 Torr; no. of scans = 1024.



Figure 14. Infrared spectrum of cyclopentane- $d_{10}$  in the radial overtone region. Resolution = 0.25 cm<sup>-1</sup>; path length = 5.25 m; vapor pressure = 20 Torr; no. of scans = 512.



Figure 15. Raman spectrum of the radial mode of cyclopentane-1,1- $d_2$ . Exciting line = 5145 Å with ~1 W at the sample; spectral bandwidth = 4 cm<sup>-1</sup>; pen period = 100 s; sensitivity = 75 cps; scan speed = 0.01 cm<sup>-1</sup>/s; maximum vapor pressure at 25 °C.

TABLE III: Infrared Subband Structure for Cyclopentane, Derived by Mills for a Pseudorotating Model<sup>a</sup>

sym	subband structure
E <sub>1</sub> ′	$\nu_0^{\rm sub} = \nu_0 + C - 2C\zeta_t - B \triangleq 2k[C - C\zeta_t - B]$
$E_1''$	$\nu_0^{\rm sub} = \nu_0 + D - C - B - 2C\zeta_{23} + 2C\zeta_1 \pm (2\lambda[D - C\zeta_{23}] + 2k[C$
	$-C\zeta_{23}+C\zeta_{1}-B]$
$E_{2}'$	$\nu_0^{\rm sub} = \nu_0 + D \pm \{2\lambda D + 2k[C\zeta_1 - C\zeta_{23}]\}$
$E_2''$	$\nu_0^{\text{sub}} = \nu_0 + D + C - B + C\zeta_{23} + 2C\zeta_1 = \{2\lambda[D + C\zeta_{23}] - 2k[C]\}$
	$+ C\zeta_{23} + C\zeta_{1} - B]$
	Pure Pseudorotation
$E_2^{\prime\prime}$	$\nu_0^{\rm sub} = \nu_0 + 4D + C - B + 4C\zeta_{23} = \{4\lambda [D + 1/2C\zeta_{23}] - 2k[C + 1/2C\zeta_{23}] - 2k[$
-	$2C_{23} - B$

<sup>a</sup>The notation of Mills has been retained. *B* and *C* are the molecular rotational constants, *D* is the pseudorotational constant (*B* in the text),  $\zeta$ 's are the vibration-rotation Coriolis cross terms; *k* is the rotational quantum number and  $\lambda$  is the pseudorotational quantum number (*l* in the text).

The hydrogen atom positions were found by using the bisector model. A detailed description of such calculations has been previously published.<sup>39</sup>

The reduced masses calculated for all five isotopes are listed in Table II as a function of phase angle. The reduced masses for the  $d_0$  and  $d_{10}$  must necessarily be equal at any value of the phase angle since the vibrations are degenerate. For the  $d_1$ ,  $d_2$ , and  $d_6$ molecules  $\phi = 0^\circ$  represents a puckered conformation and  $\phi =$ 90° represents a twisted conformation. The calculated value of the reduced mass for cyclopentane is 29.00 amu compared to 28.1 amu calculated by Kilpatrick, Pitzer, and Spitzer.<sup>1</sup> The difference is accounted for by the fact that their model assumed that each CH<sub>2</sub> unit moved as a rigid group.

# Analysis of Data

The selection rules for a freely pseudorotating molecule were derived by Mills.<sup>38</sup> The nonrigid molecule group is isomorphic to  $D_{5h}$ ; however, the selection rules are different due to the potential energy surface for the two out-of-plane vibrations of  $E_2''$  symmetry. In the infrared, perpendicular vibrations are allowed for  $E_2''$  vibrations. The selection rules<sup>40</sup> for the pseudorotational and radial modes are  $\Delta k = \pm 1$ ,  $\Delta l = \pm 2$ , and  $\Delta r = 0$ , 1, or 2, where k is the rotational quantum number, l is the pseudorotational quantum number, and r is the radial quantum number. The selection rules for these bands in the Raman spectrum are  $\Delta l = \Delta k = 0$  and  $r = \pm 1$  and  $\pm 2$ .

Table III lists Mill's equations for the subband structure. The methylene deformation of  $d_0$  and  $d_{10}$  are cyclopentane molecules of  $A_1'$ ,  $E_1'$ , and  $E_2'$  symmetry.  $A_1'$  vibrations are inactive in the infrared and the  $E_1'$  vibrations will not show pseudorotational

<sup>(39)</sup> Laane, J.; Harthcock, M. A.; Killough, P. M.; Bauman, L. E.; Cooke,
J. M. J. Mol. Spectrosc. 1982, 91, 286.
(40) Mills does not list the r = 2 transitions, presumably because the

<sup>(40)</sup> Mills does not list the r = 2 transitions, presumably because the transition moment is expected to be very small; however, these transitions arise from the  $R^2$  term in his eq 8.

TABLE IV: Pseudorotational	Combination	<b>Bands</b> of	of Cyclo	pentane
----------------------------	-------------	-----------------	----------	---------

difference bands, cm <sup>-1</sup>						sum bands, cm <sup>-1</sup>					
				literat	ure <sup>a</sup>		<b>e</b>			literat	ure <sup>a</sup>
$\rightarrow l - 1$	obsd	splt.	$\Delta$	$l \rightarrow l - 1$	obsd <sup>b</sup>	$l \rightarrow l + 1$	obsd	splt.	Δ	$l \rightarrow l + 1$	obsd <sup>b</sup>
2-1	{ <sup>1450.2</sup> 1449.3	0.9				1-2	{ <sup>1467.5</sup> 1468.6	1.1	5.0		
3-2 4-3	1443.9 w 1439.3 b	5.8	4.6	5-4	1437.0	2-3	${1473.2 \\ 1474.5}$	1.3	5.9		
5-4	{ <sup>1434.4</sup> 1433.1	1.3	5.5	6-5	1431.2	3-4	1478.5 b (1484.8		4.6 6.5		
6-5	${1428.4 \\ 1427.0}$	1.4	6.0	7-6	1425.5	4-5	(1485.3 sh (1490.3	0.5	5.7	3-4	1482.6
7-6	${1422.6 \\ 1421.7}$	0.9	5.5	8-7	1420.0	5-6	(1491.2)	0.9	5.0	4-5	1487.8
8-7	${1418.0 \\ 1416.8}$	1.2	4.8	9-8	1415.3	6-7	1496.3	1.1	4.8	5-6	1492.8
9-8	${1412.7 \\ 1411.3}$	1.4	5.4	10-9	1409.1	7-8	(1505.4	1.1	5.2		
10-9	{1407.7	1.4	5.0	11-10	1405.1	8-9	1506.1	0.7	4.8		
	1402.5		4.3			9-10	1510.1	1.0		8-9	1507.7

10 - 11

11 - 12

12-13

13 - 14

1511.0

1515.0

1516.5

(1521.1

1522.5

1525.5

1526.2

1530.0

<sup>a</sup>Reference 22. <sup>b</sup>Reference 8.

(1403.5

1402.0

(1398.0

1396.7

(1393.2

1392.2

1388.2

 $1 \rightarrow$ 

11 - 10

12-11

13 - 12

14-13

structure, but the  $E_2'$  vibrations should show subbands with a spacing of 2B. The band at 1460  $\text{cm}^{-1}$  has been assigned to the superposition of the  $E_1'$  and  $E_2'$  vibrations with the fine structure coming from the  $E_2'$  vibration.

1.5

1.3

1.0

4.3

5.4

4.7

4.5

12-11

13-12

14 - 13

1400.0

1395.0

1390.0

Table IV lists the observed combination bands, their differences, splittings, and assignments compared to that of Carreira and co-workers.<sup>22</sup> It is difficult to compare the two assignments since the frequencies used (as reported by Durig and Wertz<sup>8</sup>) apparently were not corrected by instrument calibration and do not agree with ours. Our spectra were taken on a Fourier transform infrared instrument which has a built-in calibration.

The splittings of about 1 cm<sup>-1</sup> in our observed spectra presumably arise from the Coriolis coupling. For our calculations we have assumed the band center to be the average of the two main components. We have not attempted to evaluate the individual Coriolis constants.

For our assignments the band center is taken to be 1458.5 cm<sup>-1</sup>. whereas 1462.8 cm<sup>-1</sup> was used for the assignment of Carreira and co-workers. The band center cannot be determined absolutely. The pseudorotational spacings of the ground and first excited state of the deformation can be inferred from the combination bands. If B is larger (smaller) in the excited state, then the pseudorotational spacings of the excited state should increase (decrease) for larger quantum numbers compared to the ground state. There was no systematic deviation between the inferred pseudorotational spacings of the ground and excited state for either assignment. The present assignment gives the least deviation between the inferred pseudorotational spacings of the ground and first excited state of the deformation. The average spacing of the bands is 5.21  $cm^{-1}$  for the difference bands and 5.52  $cm^{-1}$  for the sum bands  $(5.36 \text{ cm}^{-1} \text{ for both}).$ 

The assignment of the  $d_{10}$  combination bands is not straightforward because the methylene deformations are no longer isolated. For example, a methylene wag of  $E_2'$  symmetry, which should show subband structure similar to the deformation, has been assigned to 1018 cm<sup>-1</sup>. A methylene twist of  $E_2^{\prime\prime}$  symmetry has been assigned to 1005 cm<sup>-1</sup>. An  $E_2^{\prime\prime}$  vibration should show bands with a spacing of  $2(D + C\zeta_{23})$ . The  $d_{10}$  molecule has the same symmetry as the  $d_0$  and would be expected to show the same type of spectra, so the  $d_{10}$  combination bands have been assigned as combination bands with the  $E_2'$  methylene deformation at ~1060 cm<sup>-1</sup>. This is supported by what appears to be sum bands on the high-frequency side of 1060 cm<sup>-1</sup> even though they are obscured

#### **TABLE V: Observed Pseudorotational Combination Bands of** Cyclopentane-d<sub>10</sub> and Their Assignment

1.0

1.5

1.4

0.7

5.2

6.0

4.0

4.2

9 - 10

10-11

11-12

12-13

1512.5

1518.2

1532.0

1527.5

	freq, c	m <sup>-1</sup>	
$l \rightarrow l - 1$	obsd	diff	
4-3	1048.8	5.8	
5-4	1043.0	4.4	
6-5	(1039.8 ) 1037.2		
7–6	1033.8	4.8	
8-7	{1030.9	4.5	
0_8	1028.2	5.3	
10-9	1024.2	4.2	
11-10	1017.2	3.2	
12-11	1013.3	3.7	
13-12	1009.6	4.6	
15-14	1003.0	4.3	

TABL	E VI:	Observed	Ps	eudorotai	tional	Combination	Bands	of
Cyclo	pentan	e- <i>d</i> and T	heir	Tentativ	e Ass	ignment		

· · · · · · · · ·	freq, c	m <sup>-1</sup>	
$l \rightarrow l - 1$	obsd	diff	
6-5	1430.0	<i>(</i> <b>)</b>	
7-6	1424.8	5.2	
8-7	1419.5	5.3	
9–8	1415.0	4.5	
10-9	1409.8	5.2	
11-10	1405.0	4.8	
12-11	1400.5	4.5	

by other vibrations. The combination bands were assigned assuming that the band center is 1062.3 cm<sup>-1</sup> (midway between bands at 1000.7 and 1125 cm<sup>-1</sup>) and the assignment is given in Table V. Two of the bands appear to be doublets and have been assigned as such. The overall assignment must be assumed to be somewhat tentative.

The  $d_1$  molecule has C<sub>s</sub> symmetry in the planar configuration and would not be expected to follow the same selection rules as the  $d_0$ . However, the molecule is pseudorotating and the mass effect does not seem to change the selection rules significantly. This is evident from how closely the infrared and Raman spectra of the  $d_1$  resemble those of the  $d_0$  compound.<sup>28</sup> The combination bands with the methylene deformation have an average spacing

TABLE VII: Assignments of the Radial Band Transitions Observed for Cyclopentane, Cyclopentane-d, Cyclopentane-1,1- $d_2$ , Cyclopentane-1,1,2,2,3,3- $d_6$ , and Cyclopentane- $d_{10}$ , Including the Inferred and Observed Radial Overtone Frequencies

	frequency, cm <sup>-1</sup>								
	obsd	Raman	bands	inferred <sup>a</sup>	obsd IR bands				
molecule	0-1	1-2	2-3	0-2	0-2 (gas)	0-2 (solid)			
$d_0$	272.5	264.5	257.0	537.0	545.8	547.0			
$d_1$	268.0			528.0 <sup>b</sup>	~530	529.0 <sup>d</sup>			
<i>d</i> ,	261.0	252.0	244.0	513.0	~515	523.0 <sup>d</sup>			
$d_6$	240.0	228.0		468.0	~455	464.0 <sup>d</sup>			
$d_{10}$	216.0			428.0 <sup>c</sup>	427.4	428.0			

<sup>*a*</sup> Inferred from Raman data. <sup>*b*</sup> 1-2 was assumed to be 8 cm<sup>-1</sup> lower than the 0-1. <sup>*c*</sup> 1-2 was assumed to be 4 cm<sup>-1</sup> lower than the 0-1. <sup>*d*</sup> Doublets with a center at this frequency.

of 4.9 cm<sup>-1</sup>, which is assumed to be 2B as in the  $d_0$ . When the band origin is assumed to be at the band maximum of 1456.3 cm<sup>-1</sup>, then the bands are assigned as shown in Table VI.

The second series of combination bands observed for cyclopentane near 1250 cm<sup>-1</sup> apparently arises from the sum bands of the pseudorotation with the  $\nu_{17}(E_2')$  CH<sub>2</sub> wag. It is difficult to accurately determine the band origin but the spacings between all the bands are  $4.1 \pm 0.4$  cm<sup>-1</sup>. This lower value as compared to the spacings from the  $\nu_{16}(E_2')$  CH<sub>2</sub> deformation can be attributed to different pseudorotational spacings in the first excited states of the deformation and the wag. Apparently the latter are more closely spaced while the former appear to be similar to those in the ground state. The lack of observed difference bands for the  $\nu_{17}$  combinations precluded the possibility of confirming this conclusion, however. The second series of combination bands observed for cyclopentane-*d* near 1310 cm<sup>-1</sup> similarly displays a lower average spacing (3.7 cm<sup>-1</sup>) than the CH<sub>2</sub> deformation series. Moreover, the spacing is rather erratic in nature.

The radial bands in the Raman spectra were due to  $\Delta r = 1$  and  $\Delta k = \Delta l = 0$  transitions. The assignments are straightforward and are listed in Table VII. The low-frequency infrared bands in the 500-560-cm<sup>-1</sup> region, which show pseudorotational structure for cyclopentane, are clearly the double jumps ( $\Delta r = 2$ ) of the radial band. These bands had been previously assigned to the in-plane ring deformation vibration.<sup>41</sup> The ring bending is of  $E_2$ symmetry which should show combination bands similar to that of the methylene deformation, but the band shape does not resemble the  $E_2'$  parallel band observed for the methylene deformation. Also, the observed isotopic shift of 1.28 does not fit the calculated shift of 1.07 found in the normal-coordinate analysis.<sup>28</sup> These bands are too low in frequency to be assigned to methylene rocks. For these reasons and because all five molecules show a band very close to twice the radial band frequency, these bands are assigned with confidence as double jumps in the radial mode. Table VII lists the frequencies of the 0-2 radial band transitions inferred from Raman data compared to the observed gas-phase and solid-phase bands and Table VIII lists the observed frequencies for the radial overtones of the cyclopentanes. These transitions have the selection rules  $\Delta r = \pm 2$  and  $\Delta l = 0, \pm 1$ . Table IX lists the observed and calculated frequencies for the fine structure of the radial overtone for the  $d_0$  and  $d_{10}$  molecules. The frequency of the peaks, based on eq 6 can be calculated by using

$$\nu_{l \to l'} = \nu_0 + B^* l^2 - B l^2 - D^* l^4 + D l^4 \tag{66}$$

where  $\nu_0$  is the frequency of the radial overtone, where *B* and *D* are the effective pseudorotational and pseudocentrifugal distortion constants, respectively, and where the star (\*) refers to the second excited state of the radial mode. Using  $\nu_0 = 546.0 \text{ cm}^{-1}$  for cyclopentane ( $\nu_0 = 427.7 \text{ cm}^{-1}$  for cyclopentane- $d_{10}$ ) and the values of the constants given in Table IX, we obtain an excellent fit with the observed data.

Pseudorotational Energy Levels. In a one-dimensional approximation, the pseudorotational energy levels will be quad-

TABLE VIII:	<b>Observed Fine Structure of the Radial Overtone for</b>	٥r
Cyclopentane,	Cyclopentane-d, Cyclopentane-1,1-d <sub>2</sub> , and	
Cyclopentane-	d 10 <sup>d</sup>	

frequency, cm <sup>-1</sup>								
$d_0$	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>10</sub>					
557.3 w	544.1 m	592.7 w	431.3 m					
551.8 s	541.5 w	579.0 s	429.2 w					
549.3 w	539.6 w	572.5 m	428.4 w					
547.3 w	536.8 m	569.6 w	427.7 s					
546.0 s	534.8 w	567.8 s	427.3 s					
544.9 s	532.6 s	561.8 s	426.7 s					
544.0 s	529.8 m	559.0 w	425.9 m					
541.7 m	528.8 m	557.3 s	425.2 m					
539.0 m	526.7 s	556.4 sh	424.2 m					
534.0 b	525.0 w	547.0 w	423.0 w					
531.4 b	523.0 w	541.7 w	421.0 w					
528.0 b	521.7 w	533.7 w						
524.0 b	518.2 w	525.6 w						
520.0 b	516.4 s	520.0 w						
516.0 b	514.3 s	517.9 w						
511.0 b	511.5 m	515.4 m						
507.0 b	510.2 m	512.0 m						
	502.4 w	506.6 w						
	496.5 w	495.8 w						

<sup>a</sup> For cyclopentane-1,1,2,2,3,3- $d_6$  the band was centered at 455 cm<sup>-1</sup>. Due to the small sample size a good spectrum could not be obtained. sh = shoulder; b = broad; s = strong; m = medium; w = weak.

TABLE IX: The Assignment of the Fine Structure Observed for the Infrared Spectrum of the Radial Overtone of Cyclopentane and Cyclopentane- $d_{10}$ 

				_
	$\Delta r = 2,$			
	$l \rightarrow l'$	obsd, $cm^{-1}$	calcd <sup>a</sup> cm <sup>-1</sup>	
	Cycl	opentane		
$\Delta l = \pm 1$	$2 \rightarrow 3$		554.1	
	$1 \rightarrow 2$	551.8	551.4	
	$0 \rightarrow 1$	547.3	547.9	
$\Delta l = 0$	$0 \rightarrow 0$	546.0 <sup>b</sup>	546.0	
	$1 \rightarrow 1$	546.0 <sup>b</sup>	545.8	
	2 -> 2	544.9	545.2	
	$3 \rightarrow 3$	544.0 <sup>b</sup>	543.9	
	4 → 4	541.7	542.0	
	$5 \rightarrow 5$	539.0 <sup>b</sup>	538.9	
$\Delta l = -1$	$1 \rightarrow 0$	544.0 <sup>b</sup>	543.9	
	$2 \rightarrow 1$	539.0 <sup>b</sup>	537.6	
	$3 \rightarrow 2$	534.0	535.4	
	4 → 3	531.4	531.2	
	$5 \rightarrow 4$	528.0	527.4	
	$6 \rightarrow 5$	524.0	523.6	
	$7 \rightarrow 6$	520.0	519.9	
	8 → 7	516.0	516.1	
	9 → 8	511.0	511.8	
	10 <b>→</b> 9	507.0	506.6	
	Cyclor	$bentane-d_{10}$		
$\Delta l = \pm 1$	$2 \rightarrow 3$		433.3	
	1 → 2	431.3	431.2	
	0 -+ 1	429.2	428.9	
$\Delta l = 0$	$0 \rightarrow 0$	427.7 <sup>b</sup>	427.7	
	$1 \rightarrow 1$	427.7 <sup>b</sup>	427.6	
	2 - 2	427.3	427.3	
	$3 \rightarrow 3$	426.7	426.8	
	4> 4	425.9	426.1	
	$5 \rightarrow 5$	425.2	425.1	
	$6 \rightarrow 6$	424.2	424.0	
	7> 7	423.0	422.8	
	$8 \rightarrow 8$	421.0	421.3	

 ${}^{a}B = 2.127 \text{ cm}^{-1}; B^{*} = 1.937 \text{ cm}^{-1}; D = 0.01210 \text{ cm}^{-1}; D^{*} = 0.0159 \text{ cm}^{-1}$  for cyclopentane.  $B = 1.30 \text{ cm}^{-1}; B^{*} = 1.20 \text{ cm}^{-1}; D = 0.0 \text{ cm}^{-1}; D^{*} = 0.0 \text{ cm}^{-1}$  for cyclopentane- $d_{10}$ .  ${}^{b}$  Frequency used twice in assignments.

ratically spaced and the pseudorotational transitions  $(l \rightarrow l + 2)$  will be evenly spaced with a spacing of 4B. A negative deviation will be observed for larger quantum numbers due to the effect of the barrier to planarity.

<sup>(41)</sup> Miller, F. H.; Inskeep, R. G. J. Chem. Phys. 1950, 18, 1519.

TABLE X: Observed and Calculated Pseudorotational and Radial Band Transitions for Cyclopentane

		frequency, cm <sup>-1</sup>					
		ot	osd	ca	lcd		
transition		$\Delta E_{l,l+2}^{a}$	$\Delta E'_{l,l+2}{}^{b}$	Ic	II <sup>d</sup>		
$E_{l+2} - E_l$	1 =						
	0 '	10.25		11.78	10.57		
	1	24.15	24.10	23.48	21.10		
	2	34.55	34.60	35.05	31.52		
	3	44.75	45.75	46.42	41.80		
	4	57.35	57.00	57.55	51.88		
	5	68.60	68.05	68.40	61.79		
	6	78.35	78.40	78.95	71.42		
	7	88.55	88.35	89.15	80.82		
	8	98.75	98.50	99.05	89.94		
	9	108.40	108.75	108.68	98.86		
	10	118.40	119.05	117.88	107.47		
	11	129.10	128.50	126.98	115.78		
	12	137.65	137.30	135.54	123.96		
$E_{r+1} - E_r$	r =						
	0	272.5°		274.18	272.25		
	1	264.5°		264.68	264.54		
	2	257.0 <sup>e</sup>		255.42	257.18		

<sup>a</sup> Inferred from combination bands. <sup>b</sup> Transitions in the first excited state of the methylene deformation, inferred from combination bands. <sup>c</sup>A = 6.1312 cm<sup>-1</sup>, B = -210.5538 cm<sup>-1</sup>. <sup>d</sup>A = 5.4262 cm<sup>-1</sup>, B = -206.3815 cm<sup>-1</sup>, no weight on pseudorotational spacings. <sup>e</sup>  $\Delta E_{r,r+1}$ 



Figure 16. Pseudorotational transitions, calculated and inferred from the  $E_2'$  methylene deformation combination bands, vs the pseudorotational quantum number.

The ground-state pseudorotational transitions for cyclopentane can be calculated from the pseudorotational combination bands by using the formula

$$\Delta E_{l,l+2} = \nu_{l+1} - \nu_{l+2,l+1} \tag{67}$$

where  $\nu$  are the frequencies of the appropriate sum and difference combination bands and  $\Delta E_{l,l+2}$  is the spacing of the *l* and *l* + 2 ground-state pseudorotational levels. The observed pseudorotational spacings, as calculated from the combination bands, are given in Table X. The average frequencies of the doublets were used in the calculations. Figure 16 shows a graph of the observed pseudorotational spacing vs the quantum number *l*. The pseudorotational spacings in the excited state of the deformation may also be obtained from the combination band data:

$$\Delta E_{l,l+2} = \nu_{l+1,l+2} - \nu_{l+1,l} \tag{68}$$

The inferred pseudorotational spacings for the first excited state are also listed in Table X. The pseudorotational levels appear to be very nearly the same in the ground and first excited state of the  $CH_2$  deformation.

TABLE XI: Observed and Calculated Pseudorotational and Radial Band Transitions for Cyclopentane-d

		frequency, cm <sup>-1</sup>				
transition		obsd	calcd I <sup>a</sup>	calcd II <sup>b</sup>	calcd III <sup>c</sup>	
$E_{l+1} - E_l$	<i>l</i> =				·	
	5	26.3	27.58	29.88	29.70	
	6	31.5	32.34	34.97	34.01	
	7	36.8	36.96	39.97	38.32	
	8	41.3	41.53	44.70	42.37	
	9	46.5	45.84	49.37	46.44	
	10	51.3	49.84	53.89	50.30	
	11	55.8	54.63	57.80	54.06	
$E_{r+1} - E_r$	r = 0	268.0	268.32	264.94	267.72	

<sup>a</sup>  $d_1$  potential, see text. <sup>b</sup>  $d_0$  potential, see text. <sup>c</sup>  $d_2$  potential, see text.

Only difference bands were observed for the  $d_1$  molecule, so the pseudorotational spacing in the ground state could not be inferred from the combination bands. If the ground-state spacings are the same as the excited-state spacings, which seems to be true for the  $d_0$ , then the inferred pseudorotational spacings are given by

$$\Delta E_{l,l+1} = \nu_0 - \nu_{l+1,l} \tag{69}$$

Table XI lists the observed pseudorotational spacings of the  $d_1$  inferred in this manner.

No attempt was made to infer the ground-state pseudorotational spacings of the  $d_{10}$  molecule from combination band data since only difference bands were observed. The assignment of the bands was arbitrary as the band center was uncertain. The average spacing of the bands was  $3.70 \text{ cm}^{-1}$  which corresponds to  $B = 1.85 \text{ cm}^{-1}$  and  $q_0 = 0.445 \text{ Å}$  for m = 45.99 amu.

Two-Dimensional Calculation. We have also determined the potential energy surfaces for the out-of-plane ring modes of the  $d_0$ ,  $d_1$ , and  $d_2$  molecules in this work. The  $d_6$  and  $d_{10}$  molecules did not yield enough data to determine a potential energy surface for their vibrations. The reduced masses used were those listed in Table II. The  $x_1$  and  $x_2$  coordinates were defined as the puckering and twisting, respectively. A maximum quantum number of 26 was used and the transformation coefficients were calculated by using  $\bar{x}_i$  calculated at 5000 cm<sup>-1</sup>. The coefficients (units of amu<sup>-1</sup> Å<sup>-2</sup>) used were

$$\gamma_1(d_0) = \gamma_2(d_0) = 2.82 \tag{70}$$

$$\gamma_1(d_1) = 2.55, \quad \gamma_2(d_1) = 2.81$$
 (71)

$$\gamma_1(d_2) = 2.34, \quad \gamma_2(d_2) = 2.81$$
 (72)

$$\gamma_1(d_6) = 1.85, \quad \gamma_2(d_6) = 2.47$$
 (73)

$$\gamma_1(d_{10}) = \gamma_2(d_{10}) = 1.78 \tag{74}$$

The best potential constants found for the  $d_0$ , using the Raman and infrared data, were  $A = 6.1312 \text{ cm}^{-1}$ ;  $B = -210.5538 \text{ cm}^{-1}$ ; C = D = E = 0. In dimensioned Cartesian coordinates the constants are  $A_1 = A_2 = 1/2C_{12} = 4100.55 \text{ cm}^{-1}/\text{Å}^4$ ;  $B_1 = B_2 =$  $-17219.09 \text{ cm}^{-1}/\text{Å}^2$ . This potential energy surface has a barrier to planarity of 1807.7 cm<sup>-1</sup> and an out-of-plane displacement of 0.458 Å. The calculated radial band transitions and pseudorotational transitions are given in Table X. This potential function, using the calculated reduced masses, fits the radial bands of the deuteriated compounds within 5 cm<sup>-1</sup> except for the  $d_6$  which differs by 10 cm<sup>-1</sup>. The potential function also predicts that B= 1.87 cm<sup>-1</sup> for the  $d_{10}$ , which agrees well with the value found by using a simple one-dimensional analysis (1.85 cm<sup>-1</sup>).

Neglecting the pseudorotational data, the  $d_0$  radial transitions are fit by using the following potential parameters: A = 5.4262cm<sup>-1</sup>; B = -206.3815 cm<sup>-1</sup>; C = D = E = 0.0 cm<sup>-1</sup>. This potential has a barrier to planarity of 1962.8 cm<sup>-1</sup> and  $q_0 = 0.482$  Å. This potential surface does not fit the pseudorotational transitions well, however. Table X lists the calculated transitions for the  $d_0$ .

The cyclopentane-*d* data are fit very well with a potential energy surface befined by  $A = 5.7867 \text{ cm}^{-1}$ ;  $B = -215.9822 \text{ cm}^{-1}$ ;  $C = 0.2445 \text{ cm}^{-1}$ ;  $D = -0.0129 \text{ cm}^{-1}$ ;  $E = 0.0000 \text{ cm}^{-1}$ . The barrier

TABLE XII: Observed and Calculated Radial Band Transitions for Cyclopentane, Cyclopentane- $d_1$ , -1,1- $d_2$ , -1,1,2,2,3,3- $d_{69}$  and - $d_{10}$ .

		frequency, cm <sup>-1</sup>				
molecule	r - r + 1	obsd	calcd I <sup>a</sup>	calcd II <sup>6</sup>	calcd III <sup>c</sup>	calcd IV <sup>d</sup>
$d_0$	0-1	272.5	272.25	274.18		
	1-2	264.5	264.54	264.68		
	2-3	257.0	257.18	255.42		
$d_1$	0-1	268.0	262.81	264.94	268.32	267.72
	1-2		255.34	255.63	260.40	260.11
	2-3		249.75	247.84	256.08	251.82
$d_2$	0-1	261.0	253.65	256.91	258.99	261.05
_	1-2	252.0	246.88	247.00	251.66	252.18
	2-3	244.0	243.33	240.68	249.58	244.34
$d_6$	0-1	240.0	227.29	229.55	232.15	236.43
•	1-2	228.0	222.92	223.23	226.93	228.62
	2-3		225.56	219.69	231.44	224.36
$d_{10}$	0-1	216.0	217.78	219.65		
	1-2		214.42	214.97		
	2-3		е	е		

 ${}^{a}d_{0}$  potential, no weight on pseudorotational spacings, see text.  ${}^{b}d_{0}$  potential, see text.  ${}^{c}d_{1}$  potential, see text.  ${}^{c}d_{2}$  potential, see text.  ${}^{c}Too$  high to be calculated.

to planarity is 1998.6 cm<sup>-1</sup> and  $q_0 = 0.472$  Å. The nonzero values of C and D are due to round-off errors in the adjustment of the potential constant. Table XI lists the calculated radial and pseudorotational transitions for the  $d_1$  molecule. The  $d_1$  potential function does not fit the  $d_2$  or  $d_6$  radial transitions appreciably better than the  $d_0$  potential functions.

Even though combination bands were not observed for the  $d_2$ , the three Q branches observed for the radial band provided enough information to determine a potential energy function for the vibrations. For the  $d_1$ ,  $d_2$ , and  $d_6$  molecules, twofold and fourfold barriers to the pseudorotation are allowed. All five potential constants were adjusted by using the  $d_2$  data and the constants found were  $A = 5.1380 \text{ cm}^{-1}$ ;  $B = -207.2405 \text{ cm}^{-1}$ ; C = -0.5572 $cm^{-1}$ ;  $D = 0.0519 cm^{-1}$ ;  $E = 0.0374 cm^{-1}$ . This potential has a twofold barrier to pseudorotation along the puckering axis of 19.7 cm<sup>-1</sup> and a fourfold barrier to pseudorotation of 30.4 cm<sup>-1</sup>. The twofold and fourfold barriers to pseudorotation could be due to pseudopotential terms arising from the reduced masses. The barrier to planarity is 2089.8 cm<sup>-1</sup>. The out-of-plane displacement along the potential minimum is 0.494 Å. This potential predicts the observed radial transitions of the  $d_1$  and  $d_6$  molecules fairly well.

Table XII summarizes the observed and calculated radial band transitions for each of the calculations.

#### Discussion

Pseudorotational combination bands were observed for the  $d_0$ ,  $d_1$ , and  $d_{10}$  molecules. Radial band transitions were observed in the Raman (single jumps) and in the far-infrared (double jumps) spectra for all five molecules.

In the  $d_0$ , pseudorotational combination bands were observed in combination with the  $E_2'$  methylene deformation and the  $E_2'$ methylene wag. Sum and difference band series were observed with the deformation, allowing the calculation of the pseudorotational spacings in both the ground and first excited state of the deformation. There appeared to be no difference between the two sets of levels (both have an approximate spacing of 5.8 cm<sup>-1</sup>, B = 2.9 cm<sup>-1</sup>). However, the spacing of the combination band series with the wag was much smaller (4.0 cm<sup>-1</sup>). The pseudorotational levels in the first excited state of the wag must differ from those of the ground state. One possible explanation for this is that the motion of the atoms during the pseudorotation vibration involve a wagging motion of the hydrogens. The  $d_1$  molecule also showed the same effect. The  $d_1$  combination band series with the CH<sub>2</sub> deformation had a spacing of 5.0 cm<sup>-1</sup> while the combination band series with the wag had an average spacing of 3.7 cm<sup>-1</sup>.

The combination bands observed in the  $d_{10}$  were assigned as combination bands with the  $E_2'$  deformation. The average spacing of the bands was 3.70 cm<sup>-1</sup> and therefore B = 1.85 cm<sup>-1</sup>. The isotopic shift predicted from the calculated reduced masses agrees very well with the observed drop in B. The isotopic shift of the radial band was also predicted well. This indicates that the vibrational model used in the reduced mass calculations is a reasonable model for the motion of the atoms during the vibration. This has been the first isotopic study of the out-of-plane ring modes of cyclopentane and the results support the pseudorotational model of cyclopentane proposed by Kilpatrick, Pitzer, and Spitzer in 1947.

The observation of the overtone of the radial mode for all five isotopes provides additional information on the pseudorotational and radial energy levels. The spectra of the  $d_1$ ,  $d_2$ , and  $d_6$  were too complicated to be assigned but an assignment was proposed for the fine structure observed for the  $d_0$  and  $d_{10}$ . This assignment predicts a drop in the pseudorotational constant from the ground state to the second excited state of the radial mode of 0.28 cm<sup>-1</sup> in the  $d_0$  and 0.10 cm<sup>-1</sup> in the  $d_{10}$ . The (0,0)  $\rightarrow$  (2,0) transition predicted from Raman data is  $9 \text{ cm}^{-1}$  lower than that observed. The Q branches in the Raman have widths of  $\simeq 5 \text{ cm}^{-1}$  and are actually band envelopes of transitions of  $\Delta r = 1$  and  $\Delta l = 0$  for l = 1, 2, 3, etc. The  $(r,0) \rightarrow (r + 1, 0)$  transition will not correspond to the band maxima. These transitions are expected on the high-frequency edge of the observed Q branches but the magnitude of the effect would be difficult to determine. The infrared radial overtones should provide better values for the frequencies of the radial transitions than the Raman data.

A two-dimensional potential energy surface was calculated to fit the radial and pseudorotational data of cyclopentane. The calculated potential surface fit the data very well. The barrier to planarity was calculated to be 1807.7 cm<sup>-1</sup> (5.16 (kcal) and the equilibrium out-of-plane displacement was calculated to be 0.458 Å. These results are within experimental error of those found by Carreira and co-workers:  $1824 \pm 50$  cm<sup>-1</sup> for the barrier and 0.47  $\pm$  0.04 Å for  $q_0$ .<sup>13</sup> The results also agree within experimental error with the results of an electron diffraction study.<sup>42</sup>

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**Registry No.** Cyclopentane, 287-92-3; cyclopentane- $d_1$ , 55980-41-1; cyclopentane- $1,1-d_2$ , 10557-41-2; cyclopentane- $1,1,2,2,3,3-d_6$ , 42403-24-7; cyclopentane- $d_{10}$ , 7426-92-8; cyclopentanone, 120-92-3; 1-cyclopentanol- $1-d_1$ , 26832-18-8; 1-cyclopentanol- $1-d_1$  tosylate, 95981-66-1; cyclopentanone-2,2,5,5- $d_4$ , 3997-89-5; 1-cyclopentanol-2,2,5,5- $d_4$ , 42403-26-9; 1-cyclopentanol-2,2,5,5- $d_4$  tosylate, 53355-61-6.

<sup>(42)</sup> Adams, W. J.; Geise, H. J.; Bartell, L. S. J. Am. Chem. Soc. 1970, 92, 5013.