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# Far-infrared spectra and two-dimensional potential energy surface of silacyclopentane and its deuterated isotopomers

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The far-infrared spectra of silacyclopentane and its  $1-d_1$  and  $1, 1-d_2$  isotopomers have been recorded and analyzed. Spectral series corresponding to the bending and twisting transitions were observed. Bend-twist combination bands and bending overtone spectra were also detected. Kinetic energy (reciprocal reduced mass) expansions were calculated for the bending and twisting motions. These were used along with a five-term two-dimensional potential energy surface in the vibrational Hamiltonian in order to calculate the energy states. The basis sets were carefully generated to ensure that these levels were accurately calculated. The potential energy surface calculation does an excellent job of reproducing the 103 observed transition frequencies. The potential surface has energy minima at twist angles of 30°. The barrier to planarity is  $2110 \pm 200$  cm<sup>-1</sup>. The bent structure, which corresponds to a saddle point on the surface, has an energy about 1500 cm<sup>-1</sup> above the twisted conformation.

# INTRODUCTION

The vibrational spectra and conformation of silacyclopentane,  $\overline{CH_2 CH_2 CH_2 CH_2 SiH_2}$ , have been of interest for two decades. In 1969 Laane<sup>1</sup> analyzed the far-infrared spectra resulting from the ring-bending vibration of this molecule in terms of a one-dimensional hindered pseudorotor potential energy function of the form

$$V = \frac{1}{2}V_2 (1 - \cos 2\Phi), \tag{1}$$

where  $V_2$  is the barrier to pseudorotation (energy difference between the bent and twisted forms) and where the phase angle  $\Phi = 0$  and  $\pi$  correspond to twisted conformations and where  $\Phi = \pi/2$  and  $3\pi/2$  correspond to bent conformations. A good fit between observed and calculated frequencies was obtained using  $V_2 = 1362 \text{ cm}^{-1}$  along with a value of of B = 1.966 cm<sup>-1</sup> for the pseudorotational constant. Durig and Willis<sup>2</sup> obtained a similar result for 1-silacyclopentane-1,  $1-d_2$ . In 1972 a vibrational analysis and force constant calculation<sup>3</sup> was carried out for silacyclopentane and its  $d_2$  isotopomer and the microwave spectra were reported four years later.<sup>4</sup> The molecule was shown to have a twisted conformation and the twisting angle was estimated to be 21°. The Raman spectrum of the twisting vibration of the undeuterated molecule was reported by Durig, Natter, and Kalasinsky<sup>5</sup> (referred to as DNK throughout the text), and these authors also reported a two-dimensional potential energy surface calculation in terms of bending and twisting coordinates. However, as will be shown later, these workers used an inadequate harmonic oscillator basis set for their energy level calculations, and their results proved to be inaccurate.

In the present study, we have recorded improved farinfrared spectra of the bending region of silacyclopentane and its  $d_2$  derivative, and we have observed, for the first time, twisting transitions near 260 cm<sup>-1</sup> in the infrared spectra of both of these isotopic forms. We have also observed bendtwist combination bands and bending overtone spectra for these molecules. In addition, we have prepared isotopic mixtures containing 1-silacyclopentane-1- $d_1$ , and determined the bending and twisting infrared spectra of this species by spectral subtraction. All of these data were then analyzed in terms of a two-dimensional potential energy surface. To ensure the accuracy of the results, we have calculated kinetic energy (reciprocal reduced mass) expansions for the bending and twisting vibrations for each isotopic species. We have also used basis set functions which are concentrated in the regions of the potential energy minima; this procedure resulted in accurate calculations of the vibrational energy states.

# EXPERIMENTAL

### **Preparation of compounds**

Silacyclopentane- $d_0$  and 1-silacyclopentane- $1, 1-d_2$ were synthesized from 1,1-dichloro-1-silacyclopentane<sup>6</sup> by reduction with lithium aluminum hydride (LiAlH<sub>4</sub>) or lithium aluminum deuteride (LiAlD<sub>4</sub>) in n-butyl ether. Reduction of 1,1-dichloro-1-silacyclopentane with a 3:1 mixture of LiAlD<sub>4</sub>:LiAlH<sub>4</sub> statistically produced a sample containing  $6\% d_0$ , 38% 1- $d_1$ , and 56% 1,1- $d_2$ . This mixture was used to obtain the  $d_1$  bending hotband series. Similarly a 1:1 mixture of LiAlD<sub>4</sub>:LiAlH<sub>4</sub> statistically produced 25%  $d_0$ , 50% 1- $d_1$ , and 25% 1,1- $d_2$ . This second mixture was used to obtain the twisting spectra of the  $d_1$  species. The isotopic mixtures were characterized by nuclear magnetic resonance spectroscopy to verify structure and purity.

#### Spectroscopic measurements

Infrared spectra were recorded on a Bomem DA3.002 fourier-transform infrared interferometer and a Digilab FTS-20 interferometer. A liquid-helium-cooled, germanium bolometer was used as the detector for the Bomem instrument while a DTGS detector was utilized with the Digilab system. In the 120–360 cm<sup>-1</sup> range, a 6  $\mu$ m thick mylar beamsplitter and a glowbar source were used. In the 40–125

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cm<sup>-1</sup> region, a 25  $\mu$ m thick beamsplitter and a mercury lamp source were utilized. Spectra were recorded with resolutions ranging from 0.05 to 0.5 cm<sup>-1</sup>. Gas-phase spectra were obtained using either a Wilks multireflectance cell with adjustable path lengths from 0.75 to 21 meters, or using a fixed path 4.9 meter cell. In either case, polyethylene, which was distorted by pounding to eliminate interference fringes, was used as the window material.

#### THEORY

### **General considerations**

The two out-of-plane ring vibrations of cyclopentane can be represented in terms of either ring-bending and ringtwisting vibrations or a radial motion and a pseudorotation.<sup>7</sup> The former can be represented by cartesian coordinates whereas the latter are polar coordinates. Since the bent  $(C_2)$ and twisted  $(C_s)$  forms have very nearly the same energy, the barrier to pseudorotation (conversion from bent to the twisted conformation) is essentially nonexistent and free pseudorotation exists. Silacyclopentane, however, has a twisted conformation which is considerably lower in energy that the bent form, and a sizeable barrier to pseudorotation exists for this molecule. Our molecular mechanics calculation<sup>8</sup> predicted this barrier to be 1175 cm<sup>-1</sup> and also predicted the planar structure to be 1980 cm<sup>-1</sup> higher in energy than the twisted conformation. Because the barriers are substantial, the Cartesian coordinate representation of the two out-of-plane ring vibrations (bending and twisting) is preferable to the pseudorational model.

A planar silacyclopentane ring would have  $C_{2v}$  symmetry, and the bending and twisting vibrations would have symmetry species  $B_2$  (infrared and Raman active) and  $A_2$ (infrared inactive, Raman active), respectively. For the twisted ( $C_2$ ) form, both vibrations are both infrared and Raman active. In order to determine the two-dimensional potential energy surface in terms of the bending ( $x_1$ ) and twisting ( $x_2$ ) vibrational coordinates, we require spectroscopic data for both the bending and twisting vibrational states, and also, data for the bending levels in the twisting excited states. (These can also be thought of as twisting levels in the bending excited states.)

# Potential energy and kinetic energy functions

The Hamiltonian used to solve for the energy levels is of the same form that we have used for previous two-dimensional calculations<sup>9</sup>

$$H(x_1, x_2) = \frac{-\hbar^2}{2} \left[ \frac{\partial}{\partial x_1} g_{44} \frac{\partial}{\partial x_1} + 2 \frac{\partial}{\partial x_1} g_{45} \frac{\partial}{\partial x_2} + \frac{\partial}{\partial x_2} g_{55} \frac{\partial}{\partial x_2} \right] + V(x_1, x_2), \quad (2)$$

where the potential energy function is given by

$$V(x_1, x_2) = a_1 x_1^4 + b_1 x_1^2 + a_2 x_2^4 + b_2 x_2^2 + c x_1^2 x_2^2$$
(3)

and where  $x_1$  and  $x_2$  represent the bending and twisting vibrational coordinates. These are defined in the manner pre-



FIG. 1. Definitions of (A) the ring-bending  $(x_1)$  and (B) the ring-twisting  $[x_2 = b(z_1 - z_2) + a(z_3 - z_5)]$  vibrational coordinates.

viously described<sup>10</sup> and as shown in Fig. 1. The bending coordinate,  $x_1$ , represents half of the distance between two ring diagonals, and the ring-twisting,  $x_2$ , is given as a linear combination of out-of-plane atom displacements,

$$x_2 = b(z_1 - z_2) + a(z_3 - z_5), \tag{4}$$

where a = 0.3398 Å and b = 0.6201 Å are coefficients determined from orthogonality relationships.

The  $g_{ij}$  are the kinetic energy functions for the bending (i = j = 4), twisting (i = j = 5), and the bend-twist cross terms (i = 4, j = 5). The subscript numbering is affected by the fact that *i* and *j* values up to 3 refer to the three molecular rotations of the molecule. Thus,  $g_{44}$  corresponds to  $x_1$  and  $g_{55}$  corresponds to  $x_2$ . For symmetric vibrations each kinetic energy function has the form

$$g_{ij} = g_{ij}^{(0)} + g_{ij}^{(2)} x_k^2 + g_{ij}^{(4)} x_k^4 + g_{ij}^{(6)} x_k^6, \qquad (5)$$

where the  $g_{ij}^{(n)}$  are the expansion coefficients that describe the dependence on the vibrational coordinate  $x_k$ .



FIG. 2. Far-infrared spectrum of the ring-bending of silacyclopentane. Va por pressure: 70 torr; pathlength 0.7 meters; resolution:  $0.05 \text{ cm}^{-1}$ .



FIG. 3. Far-infrared spectrum of the ring-bending of 1-silacyclopentane 1, 1- $d_2$ . Vapor pressure: 70 torr; pathlength 4.9 meters; resolution: 0.5 cm<sup>-1</sup>.

# RESULTS

#### **Bending bands**

The far-infrared spectrum of silacyclopentane (Fig. 2) and 1-silacyclopentane-1,  $1-d_2$  (Fig. 3) were reinvestigated. The spectrum of an isotopic mixture containing 1-silacyclopentane-1- $d_1$  (38%) and 1-silacyclopentane-1,1- $d_2$  (56%)



FIG. 4. (A) Far-infrared spectrum of a mixture of 1-silacyclopentane-1-1 $d_1$  (38%) and 1-silacyclopentane-1,1- $d_2$  (56%). Vapor pressure: 70 torr; pathlength 4.9 meters; resolution: 0.5 cm<sup>-1</sup>. (B) Computed far-infrared spectrum of 1-silacyclopentane-1-d<sub>1</sub>.

was also recorded, and the spectrum of the  $d_1$  molecule was obtained by spectral subtraction of the  $d_2$  spectrum from that of the mixture. Figure 4 shows the spectrum of the  $d_1/d_2$  mixture as well as that computed for the monodeuterated species. Since the sample also contained about 6% of the undeuterated silacyclopentane, weak bands attributable to that molecule are also evident. The  $d_1$  and  $d_2$  spectra shown were examined at a resolution of  $0.5 \text{ cm}^{-1}$ , but others were recorded at 0.05 cm $^{-1}$  resolution to add more spectral detail. Tables I, II, and III tabulate the observed frequencies of the bands. The energy states for the transitions are labelled  $(v_{\text{twist}}, v_{\text{bend}})$ . It should be noted that the twisting levels are doubly degenerate and only the even components are listed in the tables.

In addition to the single quantum jumps between the bending levels, double and triple quantum jumps were also observed for silacyclopentane and its  $d_2$  isotopic species. The observed bands for the double jumps of the  $d_0$  species are listed in Table IV and can be seen in Fig. 5. The  $d_2$  bands are listed in Table II.

#### **Twisting bands**

Far-infrared bands associated with the ring twisting of silacyclopentane were observed for the first time for all three isotopic species. These transitions are not allowed in  $C_{2\nu}$ symmetry and thus give rise to absorptions which are considerably weaker than those in the bending series. The twisting band region for silacyclopentane is shown in Fig. 6 and the frequencies are listed in Table I. The principal series has bands at 265.2, 260.5, 255.8, and 249.8 cm  $^{-1}.$  The first three frequencies were reported (within  $\pm 1 \text{ cm}^{-1}$ ) in the Raman spectrum of DNK.<sup>5</sup> In addition to the principal twisting series in the ground state of the bending, the spectrum also shows twisting bands arising from four of the bending excited states. Thus, the  $0 \rightarrow 2$  twisting transitions from the 0, 1, 2, 3, and 4 states of the bending produce five closely spaced lines from 265.2 to 262.4  $cm^{-1}$ .

Whereas eleven twisting bands were observed for the undeuterated species, only six were observed for the  $d_2$  isotopomer and these are listed in Table II. The spectra are not shown here but are available elsewhere.<sup>11</sup> The fundamental transition for the twisting occurs at 262.3  $\text{cm}^{-1}$  rather than at 259  $cm^{-1}$ , which was previously reported for the Raman spectrum. Figure 7 shows the twisting region for the isotopic mixture. In addition to several  $d_0$  and  $d_2$  bands, three transitions were observed for the  $d_1$  species and these are listed in Table III. The fundamental occurs at  $263.4 \text{ cm}^{-1}$ , intermediate between the  $d_0$  and  $d_2$  frequencies of 265.2 and 262.3  $cm^{-1}$ .

There appear to be extraneous bands throughout the spectra of the  $d_0$  species, but many of them are due to the triple quantum jumps of the bending. These have been discussed above (Table IV).

#### **Twist-bend difference bands**

Combination bands, corresponding to the differences between the twisting and bending energy states, were observed for silacyclopentane near 165 cm<sup>-1</sup>. Bands corre-

<b>Transitions</b> <sup>a</sup>	Observed	Literature <sup>b</sup>	Calc I <sup>c</sup>	Calc II <sup>d</sup>
(0,0) - (2,0)	265.2	264.5	265.2	267.9
(0,1) - (2,1)	264.2		265.1	267.3
(0,2) - (2,2)	263.6		264.7	266.3
(0,3) - (2,3)	263.1		264.0	265.0
(0,4) - (2,4)	262.4		263.2	263.4
(2,0) - (4,0)	260.5	259.9	260.5	260.5
(2,1) - (4,1)	259.9		260.6	259.9
(2,2) - (4,2)	258.8		260.2	258.8
(4,0) - (6,0)	255.8	255.3	255.7	252.3
(4,1) - (6,1)	254.6		255.9	252.0
(6,0) - (8,0)	249.8		250.6	243.4
(0,0) - (0,1)	101.75	101.7	101.75	101.8
(0,1) - (0,2)	99.45	99.6	99.4	99.4
(0,2) - (0,3)	97.2	97.3	97.1	97.0
(0,3) - (0,4)	95.0	95.0	94.9	94.7
(0,4) - (0,5)	92.6	92.6	92.6	92.3
(0,5) (0,6)	90.3	90.3	90.4	89.8
(0,6) - (0,7)	87.8	87.2	88.1	87.4
(0,7) - (0,8)	85.2	85.2	85.8	84.9
(0,8) - (0,9)	82.2	82.5	83.5	82.3
(0,9) - (0,10)	79.6		81.0	79.6
(0,10) - (0,11)	76.6		78.9	76.8
(2,0) - (2,1)	100.8	100.7	101.75	101.2
(2,1) - (2,2)	98.8	98.7	99.0	98.4
(2,2) - (2,3)	96.6	96.6	96.5	95.7
(2,3) - (2,4)	94.3	94.3	94.0	93.0
(2,4) - (2,5)	91.8	91.8	91.5	90.4
(2,5) - (2,6)	89.2	89.2	89.1	87.7
(2,6) - (2,7)	86.6	86.6	86.6	84.9
(4,0) - (4,1)	100.1	,	101.8	100.7
(4,1) (4,2)	97.7		98.6	97.3
(4,2) - (4,3)	95.5		95.7	94.2
(4,3) - (4,4)	93.1		93.1	91.2

TABLE I. Observed and calculated frequencies  $(cm^{-1})$  for ring-puckering and ring-twisting vibrations of silacyclopentane- $d_0$ .

<sup>a</sup>  $(v'_2, v'_1) - (v_2, v_1)$  where  $v_2$  and  $v_1$  are the twist and bend quantum numbers, respectively. <sup>b</sup> From Refs. 1 and 5.

°Calc I: V<sub>1</sub> =  $2.46 \times 10^4 x_1^4 - 1.26 \times 10^4 x_1^2 + 2.28 \times 10^4 x_2^4 - 1.70 \times 10^4 x_2^2 + 9.47 \times 10^4 x_1^2 x_2^2$ .

<sup>d</sup>Calc II:  $V_{II} = 1.10 \times 10^4 x_1^4 - 5.14 \times 10^3 x_1^2 + 3.68 \times 10^4 x_2^4 - 1.76 \times 10^4 x_2^2 + 1.17 \times 10^5 x_1^2 x_2^2$ .

sponding to  $\Delta v_{\text{twist}} = 2$ ,  $\Delta v_{\text{bend}} = -1$  originate from the  $v_{\text{twist}} = 0$ , 2, and 4 states (the odd components of the doubly degenerate twisting levels are not listed for the sake of clarity). These difference bands are also shown in Fig. 5 and are listed in Table V. The observed frequencies agree very closely to those predicted from the transitions listed in Table I. Several difference bands were also observed for the  $d_1$  and  $d_2$  species, and their frequencies are included in Tables II and III.

All of the transitions discussed above, except for the double and triple quantum jumps which further confirm the assignments, are shown in Figs. 8, 9, and 10 for the  $d_0$ ,  $d_1$ ,  $d_2$  compounds, respectively. The consistency of the data can be seen to be excellent.

#### CALCULATIONS

#### Selection of initial potential parameters

In the study by DNK<sup>5</sup> these workers utilized a twodimensional basis set obtained by taking the product of two one-dimensional harmonic oscillator basis sets. This proved to be a poor choice, however, because the DNK functions are concentrated near the origin where both the bending and twisting coordinates are zero (i.e.,  $x_1 = x_2 = 0$ ). The silacyclopentane molecule, however, has its energy minima and thus its wave functions concentrated near the twisting minima, well away from the origin. DNK recognized this problem to some extent in that they reported only two calculated twisting frequencies for their potential energy surface. Un-

Transitions <sup>a</sup>	Observed	Literature <sup>b</sup>	Calc I <sup>c</sup>	Calc II <sup>d</sup>	
(0,0) - (2,0)	262.3	259.0	262.4	265.3	
(0,1) - (2,1)	261.4		262.1	264.4	
(0,2) - (2,2)	261.0		261.5	263.3	
(2,0) - (4,0)	258.4		257.9	257.8	
(2,1) - (4,1)	257.9		257.6	257.0	
(4,0) - (6,0)	254.5		253.1	249.8	
(0,0) - (0,1)	94.5	94.5	95.8	95.8	
(0,1) - (0,2)	92.9	92.9	93.8	93.8	
(0,2) - (0,3)	91.5	91.5	91.9	91.8	
(0,3) - (0,4)	89.9	89.9	89.9	89.7	
(0,4) - (0,5)	88.2	88.2	88.0	87.7	
(0,5) - (0,6)	86.6	86.6	86.1	85.6	
(0,6) - (0,7)	84.7	84.7	84.1	83.4	
(0,7) - (0,8)	82.7	82.2	82.1	81.3	
(2,0) - (2,1)			95.4	95.0	
(2,1) - (2,2)			93.3	92.7	
(2,0) - (0,1)	167.8		166.6	169.4	
(2,1) - (0,2)	168.5		168.3	170.6	
(4,0) - (2,1)	161.2		162.7	162.9	
(0,0) - (0,2)	187.4		189.6	189.6	
(0,1) - (0,3)	184.3		185.7	185.6	
(0,2) - (0,4)	181.1		181.8	181.5	
(0,3) - (0,5)	178.0		177.9	177.4	
(0,4) - (0,6)	174.6		174.1	173.3	
(0,5) - (0,7)	171.1		170.2	169.0	

TABLE II. Observed and calculated frequencies  $(cm^{-1})$  for ring-puckering and ring-twisting vibrations of silacyclopentane-1, 1- $d_2$ .

 ${}^{a}(v'_{2},v'_{1}) - (v_{2},v_{1})$  where  $v_{2}$  and  $v_{1}$  are the twist and bend quantum numbers, respectively. <sup>b</sup> From Ref. 5.

<sup>c</sup>Calc I:  $V_1 = 2.46 \times 10^4 x_1^4 - 1.26 \times 10^4 x_1^2 + 2.28 \times 10^4 x_2^4 - 1.70 \times 10^4 x_2^2 + 9.47 \times 10^4 x_1^2 x_2^2$ . <sup>d</sup>Calc II:  $V_1 = 1.10 \times 10^4 x_1^4 - 5.14 \times 10^3 x_1^2 + 3.68 \times 10^4 x_2^4 - 1.76 \times 10^4 x_2^2 + 1.17 \times 10^5 x_1^2 x_2^2$ .

fortunately, even these proved to be inaccurate.

In order to avoid the same pitfall, we first estimate the form of the silacyclopentane potential energy surface and then create a basis set localized in the regions of the energy minima. First, we write Eq. (3) in terms of the bending coordinate  $x_1$  at the twisting where  $x_2 = x_2^0$ :

TABLE IV. Double and triple quantum jumps  $(cm^{-1})$  of the ring bending of silacyclopentane.

	Transitions	<b>Predicted</b> <sup>a</sup>	Observed
$\Delta v_{\rm bend} = 2$			and the second
$v_{\text{twist}} = 0$	(0,0) - (0,2)	201.2	201.6
	(0,1) - (0,3)	196.6	196.3
	(0,2) - (0,4)	192.2	192.0
	(0,3) - (0,5)	187.6	187.4
	(0,4) - (0,6)	182.9	182.6
	(0,5) - (0,7)	178.1	177.9
$v_{\text{twist}} = 2$	(2,0) - (2,2)	199.6	200.3
	(2,1) - (2,3)	195.4	195.2
	(2,2) - (2,4)	190.9	190.6
	(2,3) - (2,5)	186.1	185.8
	(2,4) - (2,6)	181.0	180.9
	(2,5) - (2,7)	175.8	175.5
$v_{\rm twist} = 4$	(4,0) - (4,2)	197.8	198.0
	(4,1) - (4,3)	193.2	193.0
	(4,2) - (4,4)	188.6	188.8
$\Delta v_{\rm bend} = 3$			
$v_{\rm twist} = 0$	(0,0) - (0,3)	298.5	298.4
	(0,1) - (0,4)	291.7	291.7
	(0,2) - (0,5)	284.8	285.0
	(0,3) - (0,6)	278.0	277.9
	(0,4) - (0,7)	270.7	270.6
	(0,5) - (0,8)	263.3	263.1
	(0,6) — (0,9)	255.3	255.4

TABLE III. Observed and calculated frequencies  $(cm^{-1})$  for ring-puckering and ring-twisting vibrations of silacyclopentane-1- $d_1$ .

Transitions	Observed	Calc I	Calc II	
(0,0) - (2,0)	263.4	263.7	266.6	
(0,1) - (2,1)	262.3	263.5	265.8	
(2,0) - (4,0)	259.3	259.2	259.1	
(0,0) - (0,1)	97.8	98.5	98.5	
(0,1) - (0,2)	96.0	96.4	96.4	
(0,2) - (0,3)	94.2	94.3	94.2	
(0,3) - (0,4)	92.5	92.2	92.0	
(0,4) - (0,5)	90.5	90.1	89.8	
(0,5) - (0,6)	88.3	88.1	87.6	
(0,6) - (0,7)	86.2	86.0	85.4	
(0,7) - (0,8)	84.0	83.7	82.7	
(2,0) - (0,1)	165.6	165.2	168.0	
(2,1) - (0,2)	167.1	167.2	169.4	



FIG. 5. Far-infrared spectrum of silacyclopentane from 145 to 205 cm<sup>-1</sup> showing the twist-bend difference bands and the double quantum jump spectrum. Vapor pressure: 70 torr; pathlength 20.2 meters; resolution: 0.25 cm<sup>-1</sup>.



FIG. 7. Far-infrared spectrum of the ring-twisting region of an isotopic mixture of the  $d_0$  (25%),  $d_1$  (50%), and  $d_2$  (25%) silacyclopentane species. Vapor pressure: 70 torr; pathlength 20.2 meters; resolution: 0.25 cm<sup>-1</sup>.

$$V(x_1, x_2^0) = a_1 x_1^4 + [b_1 + c(x_2^0)^2] x_1^2 + K_T, \qquad (6)$$

where

$$K_T = a_2(x_2^0)^4 - b_2(x_2^0)^2 \tag{7}$$

is a constant. The potential function in terms of  $x_2$  for  $x_1 = 0$ (no bending) is

$$V(0,x_2) = a_2 x_2^4 + b_2 x_2^2 \tag{8}$$

and, therefore, by setting  $(dV/dx_2) = 0$  we find that

$$x_2^0 = (-b_2/2a_2)^{1/2}.$$
 (9)



FIG. 6. Far-infrared spectrum of the ring-twisting region of silacyclopentane. Vapor pressure: 70 torr; pathlength 20.2 meters; resolution: 0.25 cm<sup>-1</sup>.

The twisting barrier is  $b_2^2/4a_2$ . It is assumed that  $b_2$  is negative for the nonplanar (twisted) ring and that  $c(x_2^\circ)^2 = -cb_2/2a_2 > |b_1|$ . This means that at  $x_2 = x_2^\circ$  the minimum bending energy occurs at  $x_1 = 0$ .

The twisting angle, defined as the angle between the  $C_{\alpha} \operatorname{SiC}_{\alpha}$  and  $C_{\beta} \operatorname{SiC}_{\beta}$  planes of silacyclopentane, has been estimated from its microwave spectrum<sup>4</sup> to be 21° and this corresponds to  $x_2^{\circ} = 0.34$  Å according to our definition of  $x_2$  in Fig. 1. We also have carried out molecular mechanics (MM2) calculations for this ring molecule,<sup>8</sup> and these predict a twist angle of 27° which corresponds to a value of  $x_2^{\circ} = 0.44$  Å. The calculations also give barriers to planarity

TABLE V. Twist-bend difference frequencies (cm<sup>-1</sup>) of silacyclopentane.

Transitions	Predicted <sup>a</sup>	Observed	
(0,1) - (2,0)	163.5	163.5	
(0,2) - (2,1)	164.8	164.8	
(0,3) - (2,2)	166.4	166.4	
(0,4) - (2,3)	168.0	168.1	
(0,5) - (2,4)	169.7	169.7	
(0,6) - (2,5)	171.2	171.3	
(0,7) - (2,6)	172.6	172.7	
(0,8) - (2,7)	174.0	174.0	
(0,9) - (2,8)	175.7	175.5	
(2,1) - (4,0)	159.7	159.8	
(2,2) - (4,1)	161.0	161.2	
(2,3) - (4,2)	162.1	162.9	
(4,1) - (6,0)	155.7	155.3	
(4,2) - (6,1)		157.0	
(4,3) - (6,2)		159.2	

<sup>a</sup> Based on data in Table I.



FIG. 8. Energy level diagram for silacyclopentane- $d_0$ .

and pseudorotation of 1980 and 1175 cm<sup>-1</sup> respectively. Thus, if we set  $x_2^{\circ}$  in Eq. (9) to a specific value (21° or 27°) and choose a barrier height (1980 cm<sup>-1</sup>), we can calculate initial estimates for  $a_2$  and  $b_2$ .

An alternative method for calculating initial values for  $a_2$  and  $b_2$  is to assume a one-dimensional twisting function given in Eq. (8) and then use this to fit the observed twisting data. This is most easily done by transforming the one-dimensional function (here  $x = x_2$  when twisting is considered),

$$V = ax^4 + bx^2, \tag{10}$$

to reduced (undimensioned) form

$$V = A(z^4 + Bz^2) \tag{11}$$

using the relationships<sup>12</sup>

$$A = (h^{2}/2\mu)^{2/3}a^{1/3},$$

$$B = (h^{2}/2\mu)^{1/3}a^{-2/3}b,$$
(12)
(13)

and

$$z = (2\mu/h^2)^{1/6} a^{1/6} x.$$
(14)

Thus, the 0–2 and 2–4 twisting frequencies at 265.2 and 260.5 cm<sup>-1</sup> can be used to calculate the constants A and B for a reduced one-dimensional twisting potential energy function. We find A = 18.7 cm<sup>-1</sup> and B = -26.6 cm<sup>-1</sup>. Since we have calculated the reduced mass for the twisting,  $\mu_{\text{twist}}$ , to be 31.38 au, we can estimate from Eqs. (12) and (13) that  $a_2 = 2.26 \times 10^4$  cm<sup>-1</sup>/Å<sup>4</sup> and  $b_2 = -1.73 \times 10^4$  cm<sup>-1</sup>/Å<sup>2</sup>. These values correspond to a twisting barrier of 3308 cm<sup>-1</sup> and a value for the twisting minimum of  $x_2^{\circ} = 0.62$  Å or a twist angle of 39°. As will be seen, such a one-dimensional approximation tends to overstate the twisting barrier since it does not take into account the interaction with the bending.

In order to gain some insight into the bending part of the potential surface, we again utilize the one-dimensional treat-



FIG. 9. Energy level diagram for 1-silacyclopentane-1- $d_1$ .

FIG. 10. Energy level diagram for 1-silacyclopentane-1- $d_2$ .

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inergy (cm

ment of Eqs. (10)-(14), which has often been used for ringpuckering problems. Here  $x = x_1$  for the bending motion. The bending potential at the twisting minimum given in Eq. (6) is one-dimensional in  $x_1$  and can be correlated with Eq. (10) if we let  $a = a_1$  and

$$b = b_1 + c(x_2^{\circ})^2 = b_1 - cb_2/2a_2.$$
 (15)

Here, both  $b_1$  and  $b_2$  are negative since the purely bent and purely twisted structures are lower in energy than the planar conformation, and the one-dimensional potential energy slices along  $x_2 = 0$  and  $x_1 = 0$  must each be of the doubleminimum type. The magnitude of the second (positive) term in Eq. (15) is substantially larger than  $|b_1|$  and thus b is large and positive. Laane<sup>12</sup> showed that the energy levels for this one-dimensional situation would be nearly harmonic and that the frequency of the transitions would be very close to

$$v = 2AB^{1/2},$$
 (16)

where A and B are related to a and b by Eqs. (12) and (13). As has been seen, the bending series of silacyclopentane is, in fact, nearly harmonic. The 0–1 transition is at 101.75 cm<sup>-1</sup> and the 1–2 at 99.45 cm<sup>-1</sup>. Thus, Eqs. (12), (13), (15), and (16) together with a value of v = 101.75 cm<sup>-1</sup> and  $\mu_{bend}$ = 141.0 au, can be utilized to obtain a useful relationship for estimating  $a_1$ ,  $b_1$ , and c. In addition, the prediction from molecular mechanics calculations that the purely bending barrier (for  $x_2 = 0$ ) should be near 705 cm<sup>-1</sup> allows the values of  $a_1$  and  $b_1$  to be independently estimated.

Since all of the experimental data are used to calculate the final potential energy surface, the precise values of the initial estimates for  $a_1$ ,  $b_1$ ,  $a_2$ ,  $b_2$ , and c are not too critical. However, they need to be close enough so that the general nature of the potential is correct and so that the basis functions can be selected in a manner that they are concentrated in the regions of the twisting minima.

#### **Basis functions**

After a set of initial potential energy parameters has been selected for Eq. (3), basis functions are generated that are localized near  $(0, \pm x_2^\circ)$  on the potential energy surface. This is accomplished by first using a harmonic oscillator basis set and then solving for the one-dimensional (twisting) eigenfunctions corresponding to the potential function of Eq. (8). These functions, which are dependent on  $x_2$ , are then multiplied times a separate set of harmonic oscillator functions, which have a harmonic frequency equal to the bending frequency (101.75 cm<sup>-1</sup>) and which depend on  $x_1$ . This two-dimensional basis set is then symmetry factored into four symmetry blocks corresponding to  $A_1$  (eveneven),  $A_2$  (odd-odd),  $B_1$  (even-odd), and  $B_2$  (odd-even) symmetry species. A dimension as small as 150 for each symmetry block (effectively 600 for the entire calculation) typically produces accurate energy levels. Nonetheless, the validity of the energy level calculations was confirmed by utilizing basis sets of dimension 600 for each symmetry block. We have three independent computer programs performing these calculations, and each produced identical results.

The two-dimensional harmonic oscillator basis set used by DNK<sup>5</sup> in their calculations failed to give accurate energy levels, especially for the twisting levels. This is not surprising since their functions were centered about the potential origin (0,0) rather than in the region of highest conformational probability (0,  $\pm x_2^{\circ}$ ). These authors reported calculated twisting frequencies of 264.5 and 259.6 cm<sup>-1</sup> for the two lowest transitions, but the correct values calculated for their potential should have been 263.8 and 253.3 cm<sup>-1</sup>, respectively. Such errors have a dramatic effect since a potential function with a barrier to planarity of over  $3200 \text{ cm}^{-1}$  would have been required to produce their reported calculated frequencies. The barrier reported by DNK, however, was 1558.6 cm<sup>-1</sup>. Further problems in the DNK calculations can be seen in the irregular spacing calculated for the bending series.

#### Calculation of reduced masses

As indicated earlier, it is necessary to calculate reduced masses for the out-of-plane ring vibrations in order to relate the calculated vibrational potential functions to the actual conformations of the molecule. The methods used to calculate the reduced masses for the bending and twisting are the same as previously described for five-membered rings.<sup>10</sup> The structural parameters were determined from a molecular mechanics calculation and can be found elsewhere.<sup>11</sup> The observed frequency shift for the two vibrations upon isotopic substitution should be accounted for by corresponding changes in the kinetic energy expansions. In the case of silacyclopentane, the calculated isotope shifts using the basic bisector model account for much of the observed shifts. However, as is often the case, these simple representations of the bending and twisting motions are somewhat imperfect in accurately calculating the isotopic shifts because other vibrations can couple somewhat with the out-of-plane ring modes. In this particular case, we expect the ring-bending to be most coupled to the SiH<sub>2</sub> rocking mode and the ringtwisting to interact most with the SiH<sub>2</sub> twisting mode. The kinetic energy model is thus used to incorporate these interactions. A rocking parameter<sup>10</sup> of R = 0.07 and a twisting parameter of 0.3 were found to best reproduce the experimental shifts. The coupling of these motions to the puckering in a very small way can be looked at as a refinement to bring the calculated isotopic effects into correspondence with experiment. Table VI lists the calculated kinetic energy coefficients for the  $d_0$ ,  $d_1$ , and  $d_2$  molecules. It should be noted that the expansion for the  $d_1$  species includes odd terms due to the asymmetric substitution.

Because planar silacyclopentane has  $C_{2v}$  symmetry, the  $g_{45}$  cross term is zero for this structure. The coordinate dependence of both  $g_{45}$  and  $g_{55}$  was neglected.

The reduced masses for the bending and twisting vibrations are the reciprocals of the first terms in the kinetic energy expansions. Thus,  $\mu_{bend} = 141.0$  au and  $\mu_{twist} = 31.38$  au for silacyclopentane.

TABLE VI. Calculated kinetic energy values for the bending and twisting of silacyclopentane- $d_0$ , and silacyclopentane-1- $d_1$  and silacyclopentane-1, 1- $d_2$ . The form of the kinetic energy function is  $g_{ij} = g_{ij}^{(0)} + g_{ij}^{(2)}q_k^2 + g_{ij}^{(4)}q_k^4 + g_{ij}^{(6)}q_k^6$ . Rocking parameter = 0.07. Twisting parameter = 0.3.

Expansion term	$d_{ m o}$	$d_1$	<i>d</i> <sub>2</sub>
Bending			
<b>g</b> <sup>(0)</sup>	0.007 09	0.006 645	0.006 276
g <sup>(1)</sup>	0.0	- 0.000 363	0.0
<b>g</b> <sup>(2)</sup>	- 0.020 39	- 0.019 588	- 0.018 927
g <sup>(3)</sup>	0.0	0.001 951	0.0
8 <sup>(4)</sup>	- 0.066 26	- 0.055 707	- 0.047 301
g(5) g44	0.0	0.000 969	0.0
g(6) g44	0.419 2	0.366 3	0.324 5
Twisting			
855	0.031 868	0.031 557	0.031 256

# Calculation of the silacyclopentane potential energy surface

The assumed form of the vibrational potential energy surface for silacyclopentane and its isotopomers was given in Eq. (3). In previous work  $^{7,9,13-18}$  we have described several computer programs for calculating the energy levels for this type of potential energy surface. These programs also utilize least-squares fitting routines to refine the potential energy parameters so as to get the best fit between the observed and calculated frequencies. Because of the complexity of the potential energy surface, this refinement is far from trivial. The fitting routine may settle in on a solution that provides a least-squares fit for a certain range of parameters, but one that is not an optimal fit. Thus, no more than two of the five potential parameters in Eq. (3) can realistically be adjusted at the same time. Consequently, most of the effort in determining a potential energy surface was devoted to manual adjustment of the potential energy parameters until a fairly good frequency fit has been obtained.

The spectroscopic data for silacyclopentane extend to about  $1000 \text{ cm}^{-1}$  above the ground state so that the energy states up to this point are well established (see Fig. 8). This means that the lower energy portion of the potential energy surface which determines these energy levels can be established with reasonable certainty. The prime difficulty in determining the full surface is the determination of high barriers. This can only be done by extrapolating the trends of the potential function to higher values. The data that are most relevant for evaluating the barrier to planarity are those pertaining to the twisting transitions and those involving bending transitions in twisting excited states. The trends in frequency are more significant here than the absolute frequency values. For example, the bending transitions in the  $v_{\text{twist}} = 2$ states are shifted down in frequency by approximately one cm<sup>-1</sup> as compared to the ground state. Those in the  $v_{\text{twist}} = 4$  state are shifted another cm<sup>-1</sup> further down. In the purely twisting series the frequency shifts down  $4.7 \text{ cm}^{-1}$ ,

then another 4.7 cm<sup>-1</sup>, and then 6.0 cm<sup>-1</sup>. This reflects the anharmonicity derived from the fact that the potential energy along the twisting coordinate has a maximum at the planar conformation and the walls of the potential wells rise less steeply as the energy approaches the barrier height. As mentioned earlier, a purely one-dimensional fit to the twisting data would produce a central barrier exceeding 3200 cm<sup>-1</sup>, and experience has shown that such extrapolations produce barrier estimates that are too high.

We have carried out two separate two-dimensional potential energy surface calculations. The first (Calc I) emphasized fitting the anharmonicity of the ring-twisting motion, and the initial values for the twisting parameters were based on the one-dimensional approximation described earlier. It was expected that this calculation would produce a surface that would provide an upper limit for the estimation of the barrier to planarity. This potential surface was found to be

$$V_{\rm I} = 2.46 \times 10^4 x_1^4 - 1.26 \times 10^4 x_1^2 + 2.28 \times 10^4 x_2^4 - 1.70 \times 10^4 x_2^2 + 9.47 \times 10^4 x_1^2 x_2^2, \qquad (17)$$

This has a central barrier of  $3140 \text{ cm}^{-1}$  and twisting minima of  $x_2^\circ = 0.61 \text{ Å}$ , or  $\tau = 38^\circ$ . The frequencies calculated for this function are listed in Tables I, II, and III for Calc I for each of the isotopic species. Although the function was derived from the data for the undeuterated species, it also fits that of the  $d_1$  and  $d_2$  isotopomers quite well. One way that the function does not properly reproduce the observed data is that it does not fit the frequency decreases of the bending transitions in the twisting excited states in a satisfactory manner. Since this type of datum is sensitive to the shape of the potential surface at higher energies, this is an indication that the extrapolation of the surface in Eq. (17) to higher values is not very accurate.



FIG. 11. Vibrational potential energy surface (Calc II) for the ring-bending  $(x_1)$  and ring-twisting  $(x_2)$  of silacyclopentane. Contour lines are 200 cm<sup>-1</sup> apart.





FIG. 13. Comparison of the one-dimensional potential energy along the ring-twisting coordinate of silacyclopentane: (A) from one-dimensional fit with barrier =  $3250 \text{ cm}^{-1}$ ; (B) high barrier ( $3140 \text{ cm}^{-1}$ ) two-dimensional fit (Calc I); and (C) optimal two-dimensional fit (Calc II) with a barrier of 2110 cm<sup>-1</sup>.

FIG. 12. Three-dimensional plot of half of the vibrational potential energy surface (Calc II) for silacyclopentane.

In the second calculation (Calc II) we focused on fitting the bending transitions in the twisting excited states and placed less emphasis on the pure twisting bands. The potential surface found in this manner is

$$V_{\rm II} = 1.10 \times 10^4 x_1^4 - 5.14 \times 10^3 x_1^2 + 3.68 \times 10^4 x_2^4 - 1.76 \times 10^4 x_2^2 + 1.17 \times 10^5 x_1^2 x_2^2.$$
(18)

The barrier to planarity for this function is  $2110 \text{ cm}^{-1}$ , and the energy minima occur at  $x_2^\circ = \pm 0.49 \text{ Å}$ , or  $\tau = 30^\circ$ . The frequencies calculated for this function are also shown in Tables I, II, and III as Calc II. It is evident that the twisting frequencies separate more rapidly than in Calc I, as expected for a lower barrier to planarity. We encountered a very similar situation when we analyzed a number of cyclohexene-like molecules<sup>15-17</sup> for which the calculated ring-twisting frequencies decreased more rapidly than the observed values. This is simply a statement that it is not possible to adequately represent the twisting portion of the potential energy surface when only quartic and quadratic terms are used. However, because of the excellent fit with the observed bending frequencies for Calc II, we feel that Eq. (18) is the best representation for the overall potential energy surface. Figures 11 and 12 show two different types of representations for this surface. The barriers and twist angle calculated for this potential are in considerably better agreement with the microwave and MM2 results than is Calc I.

Table VII compares the barriers and  $x_2^\circ$  and  $\tau$  values calculated for silacyclopentane by several methods. Calc II

TABLE VII. Estimation of energy barriers  $(cm^{-1})$  and twist angle.

Determination	$E_{ m planar} - E_{ m twist}$	$E_{ m bent} - E_{ m twist}$	$x_2^{\circ}$	au	Ref.
Calc I	3140	1526	0.61	38°	This work
Calc II	2110	1509	0.49	30°	This work
One-dim. (twisting)	3214		0.70	44°	This work
One-dim. (pseudorot.)		1362			1
Microwave			0.34	21°	4
MM2	1980	1175	0.44	27°	8

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can be seen to be consistent with MM2 calculations and the one-dimensional hindered pseudorotational study. While the value of  $\tau = 30^{\circ}$  is higher than the estimated microwave value of 21°, it is much closer than the value of 38° from Calc I.

Figure 13 compares the three different calculations for  $V(0,x_2)$  for the twisting coordinate. Curve A is a one-dimensional potential energy function used to fit only the twisting frequencies. Curve B is from Calc I, the two-dimensional calculation that emphasizes the fit to the twisting bands. Curve C is from Calc II, which gives the best overall results. For these determinations, the data only goes up to about  $1000 \,\mathrm{cm}^{-1}$ . It can be seen that the overall shapes of the wells for A, B, and C below 1000 cm<sup>-1</sup> are similar and the widths of the wells are also nearly the same. The true potential function is probably a little narrower than curve C at low energies so that the calculated twisting hot bands would be increased slightly in energy. At higher energies curve C should be a reasonable representation for  $V(0,x_2)$ . Nonetheless, the calculated barrier height of 2110 cm<sup>-1</sup> has an uncertainty of about  $+200 \text{ cm}^{-1}$ .

The results here estimate the energy difference between the bent and twisted forms to be about 1500 cm<sup>-1</sup>. The onedimensional pseudorotational model, which views the bending coordinate to be the beginning of a pseudorotation and the twisting (radial) coordinate to have an infinitely high central barrier, predicted an energy difference of 1362 cm<sup>-1</sup>.

#### DISCUSSION

Two-dimensional vibrational potential energy surfaces for ring-puckering and ring-twisting coordinates have previously been calculated for cyclopentene<sup>18</sup> and the related molecules, 2,5-dihydrofuran<sup>19</sup> and silacyclopent-3-ene.<sup>13</sup> These surfaces are well defined in that the energy barriers are either small (cyclopentene) or nonexistent (2,5-dihydrofuran and silacyclopent-3-ene). Thus, sufficient data are available to extend well beyond any energy maximum and up to where the potential surface is regular in shape.

We have also determined the two-dimensional potential energy surface for the ring-bending and P-H inversion vibrations of 3-phospholene.<sup>14</sup> The barrier to planarity for this system is greater than 6000 cm<sup>-1</sup> and the nature of the surface is quite complex.

Recently we have determined potential energy surfaces for cyclohexene<sup>15</sup> and five of its oxygen or sulfur containing analogs.<sup>16,17</sup> These molecules are twisted with barriers to planarity ranging from 3500 to 4500 cm<sup>-1</sup>. These systems are similar to silacyclopentane in that the data terminate well below the top of the potential energy barrier.

This study of silacyclopentane represents only the third saturated five-membered ring molecule for which a meaningful two-dimensional potential energy surface has been determined. Cyclopentane and several deuterated derivatives were recently reexamined.<sup>7</sup> For this system there is essentially free pseudorotation and the barrier to planarity is 1808  $\text{cm}^{-1}$ . Cyclopentanone<sup>20</sup> was investigated several years ago. It is twisted with a barrier to planarity of 1800  $\text{cm}^{-1}$ . The planar form is lower in energy than any bent conformation.

Silacyclopentane<sup>5</sup> and germacyclopentane<sup>21</sup> have previously been investigated but the improper selection of basis functions for these calculations made these results unreliable. For silacyclopentane the barrier to planarity had been reported to be 1559 cm<sup>-1</sup>, but a proper calculation would have resulted in a value of about 3200 cm<sup>-1</sup>. Our present study, emphasizing the higher level twist-bend data, determined the barrier to planarity to be  $2200 \pm 200$  cm<sup>-1</sup>. The energy difference between the bent and twisted forms is 1500 cm<sup>-1</sup>. The far-infrared spectrum of thiacyclopentane has also been recorded in an attempt to determine a two-dimensional potential function.<sup>22</sup> However, the assignments made for this molecule, in particular for the ring-twisting transitions, are not compatible with the type of potential energy surface expected for this molecule.

For cyclopentane, the bent and twisted forms have almost identical conformational energies. However, the torsional forces of five  $CH_2$ - $CH_2$  interactions cause the planar form to lie about 21 kJ/mol higher in energy. The extent of bending or twisting in cyclopentane is limited by the angle strain, which increases as the molecular ring is distorted away from the planar structure. The angle strain in silacyclopentane is reduced relative to that of cyclopentane since a C-Si-C angle is more deformable than the C-C-C angle. The torsional interactions are also reduced since the barrier of the internal rotation of  $-SiH_2 - CH_2$  - is only about 60% of a  $-CH_2 - CH_2$  - internal rotation. These considerations dictate that the lowest energy conformation of silacyclopentane is the twisted form. Molecular mechanics calculations carried out on the molecule predicted energy differences between the planar, twisted, and bent forms to be similar to those calculated in this work.

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