

The Ring-Puckering Potential Energy Function and
Theoretical Calculations for Silacyclopent-2-ene-d₀
and 1,1-d₂ and the Difluoro and Dichloro Derivatives

Abdulaziz A. Al-Saadi, Niklas Meinander^{a)}, and Jaan Laane*

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

*Corresponding author email: LAANE@MAIL.CHEM.TAMU.EDU

Present Address

^{a)}Department of Technology, National Defence College, FIN 00861, Helsinki, Finland

ABSTRACT

High level *ab initio* and DFT calculations have been carried out for silacyclopent-2-ene and its 1,1-d₂, 1,1-difluoro, and 1,1-dichloro derivatives. The previously published far-infrared spectra of the ring-puckering vibration, which had been interpreted to be characteristic of a rigid planar molecule, have been reanalyzed for the hydride and 1,1-d₂ derivative. Both the spectra and the theoretical calculations show the molecule to have a small barrier to planarity. The experimental data analyzed with a Gaussian barrier produce a barrier of 49 cm⁻¹ as compared to a value of 47 cm⁻¹ computed using the CCSD/6-311++G(d,p) basis set. The experimental value for the deuteride was determined to be 41 cm⁻¹ from the one-dimensional approximation. All MP2 and DFT computations for the 1,1-difluoro derivative predict a planar structure whereas the MP2 computation when used with triple zeta basis set predicts a barrier of 13 cm⁻¹ for the chloride. Vibrational frequencies were also computed for these molecules and compared to experimental results for the characteristic frequencies for these types of molecules.

KEYWORDS: Silacyclopent-2-ene; ring-puckering; far-infrared spectra; potential energy function; *ab initio* and DFT calculations.

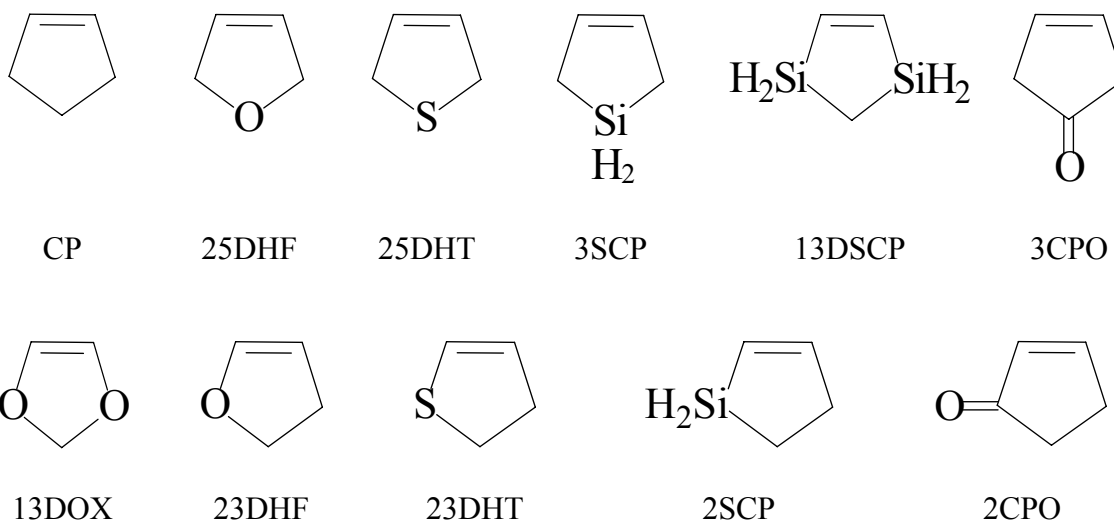
INTRODUCTION

For more than thirty years we have been investigating the potential energy surfaces governing the large-amplitude vibrations of non-rigid molecules. Both ground and excited electronic states have been studied and both experimental and theoretical methods have been applied. Some of this work has been summarized in several reviews.¹⁻⁷ Among these studies has been the investigation of “pseudo-four-membered” rings, which are five-membered rings containing one double bond each. We showed already in 1967 that molecules such as cyclopentene behaved like four-membered rings for the ring-puckering vibration since the two atoms joined by the rigid double bond moved together as one single atom.⁸ Therefore, in general, the ring puckering vibration in both four- and five-membered rings can be represented by a potential function of the form

$$V = ax^4 + bx^2, \quad (1)$$

where x is the puckering coordinate as previously defined¹⁻⁷ and where a and b are potential energy constants. As we have shown,¹⁻⁷ angle strain for these molecules contributes primarily a positive quartic (x^4) term but also contributes to some extent to the quadratic term (x^2). Torsional forces typically make a negative contribution to the b term so that the sign of b is determined by the competing angle strain and torsional forces.

The pseudo-four-membered rings previously studied are shown below. These fall into two groups, the symmetric and asymmetric molecules. The former possess C_{2v} symmetry for their planar structures whereas the asymmetric molecules only have C_s symmetry for their planar forms.



In the symmetric group of molecules cyclopentene (CP) is puckered with a barrier to planarity of 232 cm^{-1} arising from the two $\text{CH}_2\text{-CH}_2$ torsional interactions.⁸⁻¹¹ 2,5-Dihydrofuran (25DHF)¹², 2,5-dihydrothiophene (25DHT)¹³, and 3-cyclopentenone (3CPO)¹⁴ are all planar with positive a and b constants in Eq. (1) as these have no $\text{CH}_2\text{-CH}_2$ torsional interactions and angle strain dominates. Silacyclopent-3-ene (3SCP)^{15,16} and 1,3-disilacyclopent-4-ene (13DSCP)¹⁷ each have two $-\text{SiH}_2\text{-CH}_2\text{-}$ interactions, which are much weaker than the $\text{CH}_2\text{-CH}_2$ interactions, and thus make significantly less negative contribution to the b term in Eq. (1). For 3SCP this weaker torsional force almost exactly cancels out the angle strain contribution to the quadratic coefficient and a very nearly perfect quartic oscillator potential energy results. R. P. Bell in 1945 postulated that four-membered rings should have quartic potential energy functions,¹⁸ but 3SCP is the only molecule known to be close to this prediction. 13DSCP is similarly planar and has mostly a quartic potential energy function. However, there is

a small positive b constant indicating that the torsional forces are a little bit weaker and/or the angle strain is a little bit greater.

The results for 1,3-dioxole (13DOX) would appear to be out of line with the other molecules in that it has a 325 cm^{-1} barrier to planarity even though it has no $\text{CH}_2\text{-CH}_2$ torsional interactions.¹⁹ However, the non-planarity of the molecule can readily be explained by the anomeric effect resulting from the presence of the $\text{-O-CH}_2\text{-O-}$ arrangement in the molecule. Details for this have been reported.^{19,20}

Among the asymmetric molecules 2,3-dihydrofuran²¹ (23DHF) and 2,3-dihydrothiophene²² (23DHT) each have one $\text{CH}_2\text{-CH}_2$ torsional interaction which produces a barrier to planarity and a puckered structure. The barriers are 93 cm^{-1} and 430 cm^{-1} , respectively. The larger value for 23DHT reflects the fact that the presence of the “soft” sulfur atom in the ring gives rise to less angle strain. 2-Cyclopentenone²³ (2CPO) is rigid and non-planar due to conjugation between the C=O and C=C groups. However, in its $\text{S}_1(\text{n},\pi^*)$ electronic excited state it becomes much more floppy,²⁴ and in its $\text{T}_1(\text{n},\pi^*)$ state it actually takes on a puckered structure.^{25,26}

This brings us to silacyclopent-2-ene which has been difficult to understand since we first reported its far-infrared spectrum in 1970 which seemed to be indicative of a very rigid potential energy function characteristic of large angle strain or positive torsional forces.²⁷ At that time we postulated that the silicon d orbital interactions with the C=C π orbitals could result from a type of conjugation which would tend to keep the ring rigid. In 1988 we studied the far-infrared spectra of the 1,1- d_2 isotopomer of 2SCP and this appeared to confirm this rigid potential energy function.²⁸ This led us to synthesize 13DSCP with the hope of seeing great ring rigidity due to the presence of two

silicon atoms next to the double bond. Its far-infrared spectra, however, only showed a very modest increase in the stiffness of this ring.¹⁷ Until our present study, we had not been able to reconcile this apparent enigma. As the results from 2SCP have continued to seem perplexing, we have reexamined the interpretation of the 2SCP and 2SCP-d₂ spectra and also carried out high level *ab initio* calculations to better understand why the results for these molecules appeared to be out of line with all the others. Our reinterpretation of the data and the results of the theoretical calculations will be presented here.

EXPERIMENTAL

No new experimental data are presented in this work, although the original spectra were reexamined and reassigned. The experimental conditions and results were published previously.^{27,28}

COMPUTATIONS

Ab initio second-order Møller-Plesset (MP2), coupled cluster theory with single and double excitation (CCSD), and density functional theory (DFT) using the Gaussian 03 program²⁹ were employed to study the structure of silacyclopent-2-ene in its planar and nonplanar forms. The structures of the difluoro and dichloro derivatives were optimized at the MP2 level, and their frequencies were calculated. The vibrational frequencies of silacyclopent-2-ene, its 1,1-d₂ isotopomer, and the dihalo derivatives were computed using density functional theory (DFT) with the B3LYP hybrid functional using different basis sets. Because changing the basis sets used for the DFT treatments produced different results for the stable configurations of silacyclopent-2-ene, the 6-

311++G(d,p) basis set, which predicted a slightly puckered structure for silacyclopent-2-ene in agreement with the results obtained from the coupled cluster theory computations, was used to calculate the vibrational frequencies for the difluoro and dichloro derivatives.

The MP2 theory using different basis sets was utilized to locate the stable conformation of silacyclopent-2-ene and the results are shown in Table I. Smaller basis sets, which lack the diffuse and polarization functions, predicted the molecule to be totally planar. A barrier of about 50 cm^{-1} , however, was predicted when larger basis sets were used. However, for DFT calculations, even the triple-zeta basis set predicted a planar structure for silacyclopent-2-ene (Table I). The CCSD/6-311++G(d,p) calculations, which should in principle give more reliable results, confirmed that silacyclopent-2-ene is nonplanar with a puckering angle of 17° and an inversion barrier of 47 cm^{-1} . Figure 1 shows the optimized structure of silacyclopent-2-ene from the coupled cluster theory. The figure also compares the structures of the dihalo derivatives as computed at the MP2/cc-pVTZ level of theory. Table I also shows the calculated isotope shift for the 1,1-d₂ molecule from the DFT calculations. Table II shows that DFT calculations using different basis sets predict planar structures for 1,1-difluoro- and 1,1-dichlorosilacyclopent-2-ene. The MP2 theory with the triple- ζ basis set, however, predicts the dichloro derivative to be slightly puckered with a low barrier (16 cm^{-1}) and predicts the difluoro molecule to be planar. The calculated ground state structures of the dihalo derivatives were confirmed by calculating their vibrational frequencies.

New kinetic energy expressions for the ring-puckering of the 2-ene and its 1,1-d₂ isotopomer were calculated based on the optimized structure of the planar conformation determined from the CCSD/6-311++G(d,p) calculation. A program previously

described³⁰ was used to generate the kinetic energy terms. These were then used to obtain the revised potential energy functions in terms of the ring-puckering coordinates for the two molecules.

RESULTS AND DISCUSSION

Structures. The calculated structures for silacyclopent-2-ene (2SCP) and its 1,1-difluoro and 1,1-dichloro derivatives are shown in Figure 1. For the hydride the coupled cluster calculation was used to compute the structure shown whereas for the halogenated molecules the results from the MP2/triple ζ calculation are shown. For 2SCP, as expected, the smaller C–Si–C angle (93.3°) at the silicon atom as compared to the SiCC and CCC= angles at the saturated carbon atoms (105.2° and 109.8°) reflects the fact that the smaller angle bending constant at the silicon atom allows most of the angle strain to be taken on at this position even though each of these angles “prefers” to be tetrahedral. It should also be noted that the =C–Si– bond distance of 1.869 \AA vs 1.898 \AA for the –Si–CH₂– distance suggests some increased interaction between the silicon atom and the carbon-carbon double bond. This will be further discussed in the Conclusions. The calculations also predict that the parent hydride is puckered with a dihedral angle of 17° . Similarly, the chloride has a calculated puckering angle of 16° , but the fluoride is predicted to be planar. Apparently the lower energy 2p orbitals in fluorine atoms can interact in a way to stabilize the planar structure whereas the 3p orbitals on the chlorines are too high in energy. The barriers to planarity for the hydride and dichloride were calculated to be 47 and 13 cm^{-1} , respectively. The puckering of 2SCP will be discussed in detail below.

Ring-Puckering Potential Energy Function for 2SCP. As mentioned above, the ring-puckering potential energy function previously proposed for 2SCP and its 1,1-d₂ derivative appeared to be out of line with results for other five-membered ring molecules. After completing our *ab initio* calculations for 2SCP, which predicted a barrier of 47 cm⁻¹ and a puckering angle of 17°, it gave us further impetus to reexamine our earlier analyses of the spectra. It should be noted that 2SCP and 3SCP are difficult to prepare and to separate.^{15,16,27,28,31} First a mixture of the corresponding dichlorides must be synthesized and then separated by fractional distillation. The boiling points for the dichlorides are only 4° apart (137° and 141°) so their complete separation even using a spinning band distillation column is difficult to achieve. This is especially true because the dichlorides must be conserved as much as possible since they serve as starting materials for preparing 2SCP and 3SCP. The net result is that each sample winds up with about 95% purity. The 3SCP has a very intense far-infrared spectrum¹¹ since the positively charged silicon participates strongly in the large-amplitude ring-puckering motion. For 2SCP the far-infrared spectrum is much weaker since its apex carbon atom with the largest amplitude of motion has only a slight charge associated with it.^{22,23} Thus, the 2SCP (95% pure sample) far-infrared spectrum possesses bands due to 3SCP that are comparable in intensity to the 2SCP bands. The 3SCP bands are primarily in the 30 to 100 cm⁻¹ region. Our published 2SCP spectra show only bands above 110 cm⁻¹. None were reported at lower values as these would have been obscured by the more intense 3SCP bands. In the observed 2SCP spectra, however, we observed a doublet at 184.0 and 184.7 cm⁻¹ which was previously ascribed to Fermi resonance. We are now convinced that these arise from two different puckering transitions, one of which is a 0→2 transition. This implies that

the 0-1 separation is 61.3 cm^{-1} but this was not observed since the 3SCP spectra obscured it. With this realization it is straightforward to reassign the 2SCP data and bring it into consistency with the other molecules studied and also with our *ab initio* calculations. In order to calculate the ring-puckering potential energy functions using the new assignments we first needed the kinetic energy (reciprocal reduced mass) expansions.¹⁻⁷ These were calculated based on the 2SCP structure in Figure 1. For the hydride the function is

$$g_{44}^{\text{H}}(x) = 0.0069801 - 0.0168419 x^2 - 0.0646870 x^4 + 0.2331390 x^6 \quad (2)$$

and for the d_2 molecule

$$g_{44}^{\text{D}}(x) = 0.0061189 - 0.0118251 x^2 - 0.0582123 x^4 + 0.1487240 x^6. \quad (3)$$

The observed far-infrared spectra for 2SCP and 2SCP- d_2 are listed in Table III along with the assignments for the ring-puckering transitions. In addition, the 0-1 energy spacings calculated from the 0-2 and 1-2 transitions for each isotopomer are shown. In past work we have typically fitted the observed data with a potential energy function of the type shown in Eq. (1) although for the C=O out-of-plane wagging of 3-cyclopentenone¹⁴ (3CPO) in its $S_1(n,\pi^*)$ excited state, we used

$$V = ax^2 + b \exp(-cx^2). \quad (4)$$

The 3CPO data showed predominantly quadratic character above the barrier which, in this case, was reproduced with the exponential term (Gaussian barrier). For 2SCP and its d_2 isotopomer it became evident that the ring-puckering frequency sequence above the barrier required both positive quartic and quadratic terms in the potential function. Hence, neither of the functions in Eqs. (1) or (2) were able to reproduce the data. We therefore adopted the function

$$V = ax^4 + bx^2 + c \exp(-dx^2) \quad (5)$$

for which the barrier is produced by the Gaussian (exponential) term and where the other two terms can reproduce the needed quartic-quadratic mix at larger x values. For 2SCP the function which best reproduces the data is

$$V_H(\text{cm}^{-1}) = 1.98 \times 10^6 x^4 + 3.06 \times 10^4 x^2 + 378.4 \exp(-177.0x^2). \quad (6)$$

This has a barrier of 49 cm^{-1} and energy minima at $x = \pm 0.053 \text{ \AA}$ or at dihedral angles of $\pm 14^\circ$. The function is shown in Figure 2 and the calculated frequencies for this potential function are shown in Table III as Calculation I. For the d_2 isotopomer the calculated function is

$$V_D(\text{cm}^{-1}) = 1.77 \times 10^6 x^4 + 4.07 \times 10^4 x^2 + 427.4 \exp(-178.0x^2) \quad (7)$$

and this has a barrier of 41 cm^{-1} and minima at $x = \pm 0.049 \text{ \AA}$ or $\pm 13^\circ$. The calculated frequencies for this function are compared to the observed values for the deuteride in Table III and the potential energy curve is shown in Figure 3. The small differences between the functions and barriers for the two isotopomers in Eqs. (6) and (7) are not unexpected as the barriers for deuterated molecules are typically slightly smaller than the undeuterated ones. Our approximation¹⁻⁷ that the ring-puckering vibration is totally independent of all other vibrational motions gets somewhat worse for heavier molecules and this accounts for these observations.

As can be seen in Table III, the frequency agreement between observed and calculated values is excellent, indicating that the one-dimensional model is sufficiently reliable for representing the ring-puckering motion and for calculating the energy difference between the planar and puckered forms. In order to demonstrate that the form of the potential function in Eq. (1) is inadequate for representing the ring-puckering, we

nonetheless utilized this to see how well it could reproduce the spectra. This is shown in Table III as Calculation II for both isotopomers. The frequency fit at lower energies is not bad but gets progressively worse at higher energies since the mixed quartic-quadratic character can not be reproduced. Figure 4 compares the functions from Calculations I and II along with the calculated energy levels. Both do a good job of determining the lowest few levels, the barrier, and the energy minima. However, at larger x values the function in Eq. (1), the dotted curve, has too much quartic character and the potential energy increases too rapidly driving up the energies of the calculated states.

Figure 5 compares our new results for 2SCP to the ring-puckering potential energy functions of the other asymmetric five-membered rings 23DHF, 23DHT, and 2CPO. All of these except 2CPO are somewhat puckered with barriers to planarity. The 2CPO has strong conjugation between the carbonyl group and the C=C double bond and this results in a rigid planar system. The 23DHT molecule with sulfur has the highest barrier to planarity since the CSC angle bending constant is small and gives rise to less angle strain. While both 23DHF and 2SCP have small barriers to planarity, the 2SCP has a much stiffer function indicating that even though it is non-planar, there are interactions which make it difficult for the ring to pucker far from its planar conformation. These very likely do involve the silicon orbital interactions with the carbon-carbon double bond.

Figure 6 compares the ring-puckering potential function of 2SCP to the other two cyclic silanes 3SCP and 13DSCP. The 3SCP has no possibility of silicon atom interaction with the carbon-carbon double bond and only has two weak SiH₂-CH₂ torsional interactions which almost perfectly cancel out the angle strain in the quadratic term (b constant) in Eq. 1. Hence, this is a planar but floppy molecule with a nearly

perfect quartic potential energy function. 13DSCP also possesses two SiH₂-CH₂ torsional interactions but also has the possibility of Si/C=C interactions. This molecule is also planar but is somewhat stiffer probably due to the extra Si/C=C interaction. The 2SCP molecule possesses one larger CH₂-CH₂ interaction and one SiH₂-CH₂ interaction which produce the small barrier to planarity. However, of the three, this molecule then has the greatest resistance to puckering when the dihedral angle is increased to larger values. Apparently, the silicon double bond interaction accounts for that.

For 1,1-difluoro- and 1,1-dichlorosilacyclopent-2-ene the ring puckering vibration is strongly coupled to the SiX₂ (X = F or Cl) rocking and twisting vibrations which are also of low frequency. Hence, the one-dimensional model for the puckering is no longer valid and the puckering spectra can not be analyzed to determine the potential energy function. However, we have carried out calculations for both these molecules. As shown in Table II the DFT calculations using different basis sets predict planar structures for 1,1-difluoro- and 1,1-dichlorosilacyclopent-2-ene. The MP2 theory with the triple- ζ basis set, however, predicts the dichloro derivative to be slightly puckered with a low barrier (16 cm⁻¹). However, the difluoro molecule is again calculated to be planar.

Vibrational Spectra.

Many of the characteristic frequencies of 2SCP and its 1,1-difluoro- and 1,1-dichloro derivatives have been previously reported.^{30,31} These are shown in Table IV and are compared to the frequencies calculated using the B3LYP/6-311++(d,p) for these molecules in the present one. As can be seen, even though the experimental values are only accurate to ± 5 cm⁻¹, the agreement is excellent. The vibrational descriptions in the

table also help to elucidate why these vibrations are the most useful for characterizing these asymmetric five-membered rings.

CONCLUSIONS

The experimental data for the two isotopomers of 2SCP along with the theoretical calculations show this ring molecule to have a small barrier to planarity of about 49 cm^{-1} (0.14 kcal/mole). The highly rigid nature of the previously proposed potential energy function has been shown to be invalid. Nonetheless, 2SCP is considerably more rigid than the analogous oxygen (23DHF) and sulfur (23DHT) molecules. This does appear to reflect the fact that there is some interaction between the silicon orbitals and the carbon-carbon double bond. This is smaller than previously proposed, but it is still present, and the result is consistent with the modest silicon/C=C bond interaction we previously observed for 13DSCP.

ACKNOWLEDGEMENTS.

The authors wish to thank the National Science Foundation (Grant CHE-0131935) and the Robert A. Welch Foundation (Grant A-0396) for financial support.

REFERENCES

- (1) J. Laane, *J. Pure and Appl. Chem.*, **59**, 1307-1326 (1987).
- (2) J. Laane, in Structures and Conformations of Non-Rigid Molecules. J. Laane and M. Dakkouri (eds.), Kluwer Publishing, Amsterdam, pp. 65-98, 1993.
- (3) J. Laane, *Annu. Rev. Phys. Chem.*, **45**, 179-211 (1994).
- (4) J. Laane, *Intl. Rev. in Phys. Chem.*, **18**, 301-341 (1999).
- (5) J. Laane, in *Structure and Dynamics of Electronic Excited States*, J. Laane, H. Takahashi, and A. Bandrauk (eds.), Springer, Berlin, Germany, pp. 3-35 (1999).
- (6) J. Laane, *J. Phys. Chem. A* **104**, 7715 (2000) and references therein.
- (7) J. Laane, Z. Arp, S. Sakurai, K. Morris, N. Meinander, T. Klots, E. Bondoc, K. Haller, and J. Choo, in Low-Lying Potential Energy Surfaces, M. Hoffman and K. Dyall (eds.), ACS Symposium Series **828**, Washington, D.C., pp. 380-399 (2002).
- (8) J. Laane and R. C. Lord, *J. Chem. Phys.*, **47**, 4941-4945 (1967).
- (9) J. R. Villarreal, L. E. Bauman, J. Laane, W. C. Harris, and S. F. Bush, *J. Chem. Phys.*, **63**, 3727-30 (1975).
- (10) J. R. Villarreal, L. E. Bauman, and J. Laane, *J. Phys. Chem.*, **80**, 1172-1177 (1976).
- (11) L. E. Bauman, P. M. Killough, J. M. Cooke, J. R. Villarreal, and J. Laane, *J. Phys. Chem.*, **86**, 2000-2006 (1982).

- (12) L. A. Carreira, R. C. Lord, J. Chem. Phys. **51**, 3225 (1969).
- (13) T. Klots, S. N. Lee, J. Laane, J. Phys. Chem., **103**, 833-837 (1999).
- (14) J. D. Lewis and J. Laane, J. Mol. Spectrosc., **53**, 417-427 (1974).
- (15) J. Laane, J. Chem. Phys., **50**, 776-782 (1969).
- (16) P. M. Killough and J. Laane, J. Chem. Phys., **80**, 5475-5548 (1984).
- (17) L. C. Colegrove and J. Laane, J. Phys. Chem., **95**, 6494-6499 (1991).
- (18) R. P. Bell, Proc. Roy. Soc. London, **183A**, 328 (1945).
- (19) E. Cortez, R. Verastegui, J. R. Villarreal, and J. Laane, J. Amer. Chem. Soc., **115**, 12132-12136 (1993).
- (20) D. Suarez, T. L. Sordo, J. A. Sordo, J. Am. Chem. Soc., **118**, 9850 (1996).
- (21) D. Autrey and J. Laane, J. Phys. Chem., **105**, 6894-6899 (2001).
- (22) T. Klots, E. Bondoc, J. Laane, J. Phys. Chem., **103**, 8772-8776 (1999).
- (23) C. M. Cheatham and J. Laane, J. Chem. Phys., **94**, 5394-5401 (1991).
- (24) C. M. Cheatham and J. Laane, J. Chem. Phys., **94**, 7734-7743 (1991).
- (25) N. Pillsbury, J. Choo, J. Laane, and S. Drucker, J. Phys. Chem. A, **107**, 10648-10654 (2003).
- (26) J. Choo, S. Kim, S. Drucker, and J. Laane, J. Phys. Chem. A, **107**, 10655-10659 (2003).

(27) J. Laane, *J. Chem. Phys.*, **52**, 358-360 (1970).

(28) M. B. Kelly and J. Laane, *J. Phys. Chem.*, **92**, 4056-4059 (1988).

(29) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, revision C.2, Gaussian, Inc., Wallingford CT, (2004).

(30) R. A. Benkeser, Y. Nugai, J. L. Noe, R. F. Cunico, P. H. Gund, *J. Am. Chem. Soc.*, **86**, 2446 (1964).

(31) T. H. Chao, S. L. Moore, J. Laane, *J. Organometal. Chem.*, **33**, 157 (1971).

FIGURE CAPTIONS

Figure 1. Structure of silacyclopent-2-ene (2SCP) from the coupled cluster theory with single and double excitation calculations (CCSD) using the 6-311++G(d,p) basis set. Also shown are the 1,1-difluoro and 1,1-dichloro derivative structures from the MP2/cc-pVTZ calculation.

Figure 2. Ring-puckering potential energy function for 2SCP showing the observed transitions.

Figure 3. Ring-puckering potential energy function for 2SCP-d₂ showing the observed transitions.

Figure 4. Comparison of 2SCP potential energy functions and energy levels from Eq. (6) with the Gaussian barrier (solid line) and the mixed quartic-quadratic function of Eq. (1) (dotted line).

Figure 5. Comparison of ring-puckering potential energy functions of several asymmetric five-membered ring molecules.

Figure 6. Ring-puckering potential energy functions of three cyclic organosilanes.

Table I. Conformational energies, barriers, and puckering frequencies for silacyclopent-2-ene from different basis sets.

Theory	Total energies (Hartree)		Puckering angle (deg.)	Puckering frequency ^b (cm ⁻¹)	Barrier (cm ⁻¹)
	Puckered	Planar			
MP2/3-21G			0°	9	0
MP2/6-31G			0°	27	0
MP2/6-31+G(d)	-445.6285629	-445.6282456	19°	99	70
MP2/6-311++G(d,p)	-445.7689100	-445.7685439	20°	102	80
MP2/cc-pVTZ	-445.8977514	-445.8975197	18°	91	51
CCSD/6-311++G(d,p)	-445.8251234	-445.8249104	17°	---	47
DFT-B3LYP/3-21G			0°	47	0
DFT-B3LYP/6-31G			0°	53	0
DFT-B3LYP/6-31+G(d)	-446.7245222	-446.7245127	9°	45 (46) ^a	2
DFT-B3LYP/6-311++G(d,p)	-446.7880437	-446.7880384	8°	38 (36)	1
DFT-B3LYP/cc-pVTZ			0°	19 (17)	0
DFT-B3LYP/6-311++G(3d2f,2pd)			0°	13	0
Experimental ^c			14° (13°)	61 (60)	49 (41)

^aValues in parentheses are for the 1,1-d₂ isotopomer.

^bScaling factors of 0.985 and 0.920 used to scale the frequencies obtained from DFT-B3LYP and MP2 calculations, respectively.

^cAs determined from this work.

Table II. Calculated barriers and ring-puckering frequencies^a (cm⁻¹) of 1,1-difluoro- and 1,1-dichlorosilacyclopent-2-ene.

	1,1-Difluoro- silacyclopent-2-ene			1,1-Dichloro- silacyclopent-2-ene		
	Puckering angle	Puckering frequency	Barrier	Puckering angle	Puckering frequency	Barrier
MP2/cc-pVTZ	0°	13	0°	16°	9	13
DFT-B3LYP/6-31+G(d)	0°	57	0°	0°	20	0
DFT-B3LYP/6-311++G(d,p)	0°	56	0°	0°	20	0
DFT-B3LYP/cc-pVTZ	0°	57	0°	0°	31	0

^aWith scaling factors 0.984 and 0.920 for the DFT-B3LYP and MP2 results.

Table III. Observed and calculated ring-puckering transitions (cm^{-1}) for silacyclopent-2-ene.

Transition	Observed		Calculation I ^a			Calculation II ^b		
	Frequency	Relative Intensity	Frequency	Δ	Relative Intensity	Frequency	Δ	Relative Intensity
1-Silacyclopent-2-ene								
0-1	(61.2) ^c		61.7	+0.5	0.4	60.0	-1.2	0.4
1-2	123.7	1.0	124.5	+0.8	1.0	122.4	-1.3	1.0
2-3	139.3	0.9	137.3	-2.0	0.8	140.6	+1.3	0.9
3-4	155.6	0.8	154.4	-1.2	0.7	160.9	+5.3	0.7
4-5	167.6	0.7	166.4	-1.2	0.5	176.7	+9.1	0.4
5-6	177.4	0.5	176.4	-1.0	0.4	190.4	+13.1	0.3
6-7	184.0	0.4	185.0	+1.0	0.3	----	----	----
7-8	192.1	0.2	192.6	+0.5	0.2	----	----	----
8-9	199.2	0.1	199.4	+0.2	0.1	----	----	----
0-2	184.9	0.2	186.2	+1.3	0.1			
1-Silacyclopent-2-ene-1,1-d ₂								
0-1	(60.2) ^d	----	61.0	0.8	0.4	57.1	-3.1	0.4
1-2	116.7	e	117.6	0.9	1.0	115.2	-1.5	1.0
2-3	131.2	e	130.2	-1.0	0.7	132.6	+1.4	1.0
3-4	145.9	e	145.6	-0.3	0.4	151.6	+5.7	0.7
4-5	156.8	e	156.5	-0.3	0.2	166.6	+9.8	0.5
5-6	165.0	e	165.4	+0.4	0.1	179.5	+14.5	0.3
6-7	172.9	e	173.1	+0.2	0.06	----	----	----
0-2	176.9	e	176.9	0.0	----			

^a Calculation I $V_H(\text{cm}^{-1}) = 1.98 \times 10^6 x^4 + 3.06 \times 10^4 x^2 + 3.78 \times 10^2 \exp(-177.0x^2)$

$V_D(\text{cm}^{-1}) = 1.77 \times 10^6 x^4 + 4.07 \times 10^4 x^2 + 4.27 \times 10^2 \exp(-178.0x^2)$

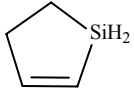
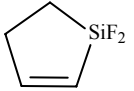
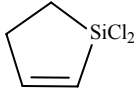
^b Calculation II $V_H(\text{cm}^{-1}) = 4.88 \times 10^6 x^4 - 3.00 \times 10^4 x^2$; $V_D(\text{cm}^{-1}) = 4.95 \times 10^6 x^4 - 2.66 \times 10^4 x^2$

^c Calculated from $\nu(0-2) - \nu(1-2) = 184.9 - 123.7 \text{ cm}^{-1}$

^d Calculated from $\nu(0-2) - \nu(1-2) = 176.9 - 116.7 \text{ cm}^{-1}$

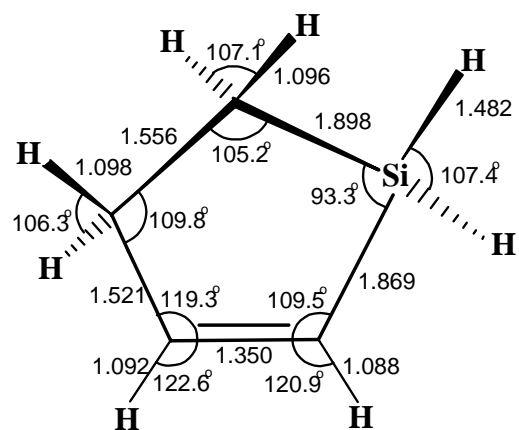
^e Quantitative data not available

Table IV. Infrared assignments of the characteristic frequencies^{a,b} of silacyclopent-2-ene and its 1,1-difluoro and 1,1-dichloro derivatives.

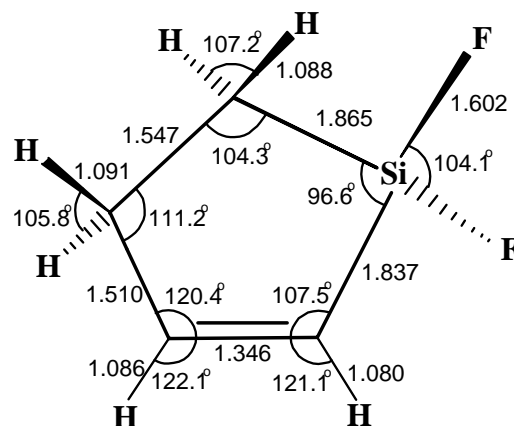
						Assignments
Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
2990	2993 (16)	3020	3005 (16)	3020	3006 (15)	CH str.
2900	2892 (22)	2940	2905 (17)	2930	2905 (19)	CH ₂ sym. str.
1560	1595 (17)	1570	1590 (30)	1560	1592 (26)	C=C str.
1440	1461 (6)	1440	1457 (15)	1440	1456 (11)	CH ₂ def.
1320	1324 (4)	1320	1331 (19)	1320	1324 (8)	CH wag (o.p.)
1140	1162 (8)	1160	1169 (25)	1150	1169 (15)	CH ₂ wag
1100	1108 (2)	1100	1111 (8)	1100	1108 (1)	CH wag (i.p.)
990	971 (65)					SiH ₂ rock
		990	983 (16)	990	983 (10)	Ring mode
870	868 (47)	840	858 (100)	830	821 (29)	Ring mode
700	715 (34)	710	687 (10)	760	732 (40)	Ring mode

^aExperimental frequencies ($\pm 5 \text{ cm}^{-1}$) are taken from Refs 30 and 31. Calculated frequencies are from the B3LYP/6-311++G(d,p) calculation using a scaling factor of 0.984 (0.964 for C-H stretches).

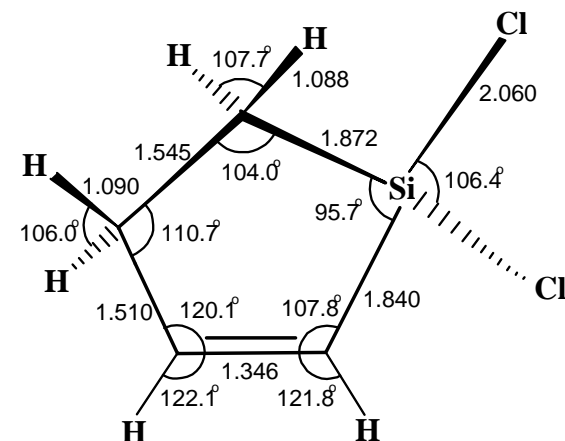
^bNumbers in parentheses are the calculated relative infrared intensities.



Silacyclopent-2-ene



Difluorosilacyclopent-2-ene



Dichlorosilacyclopent-2-ene

Figure 1.

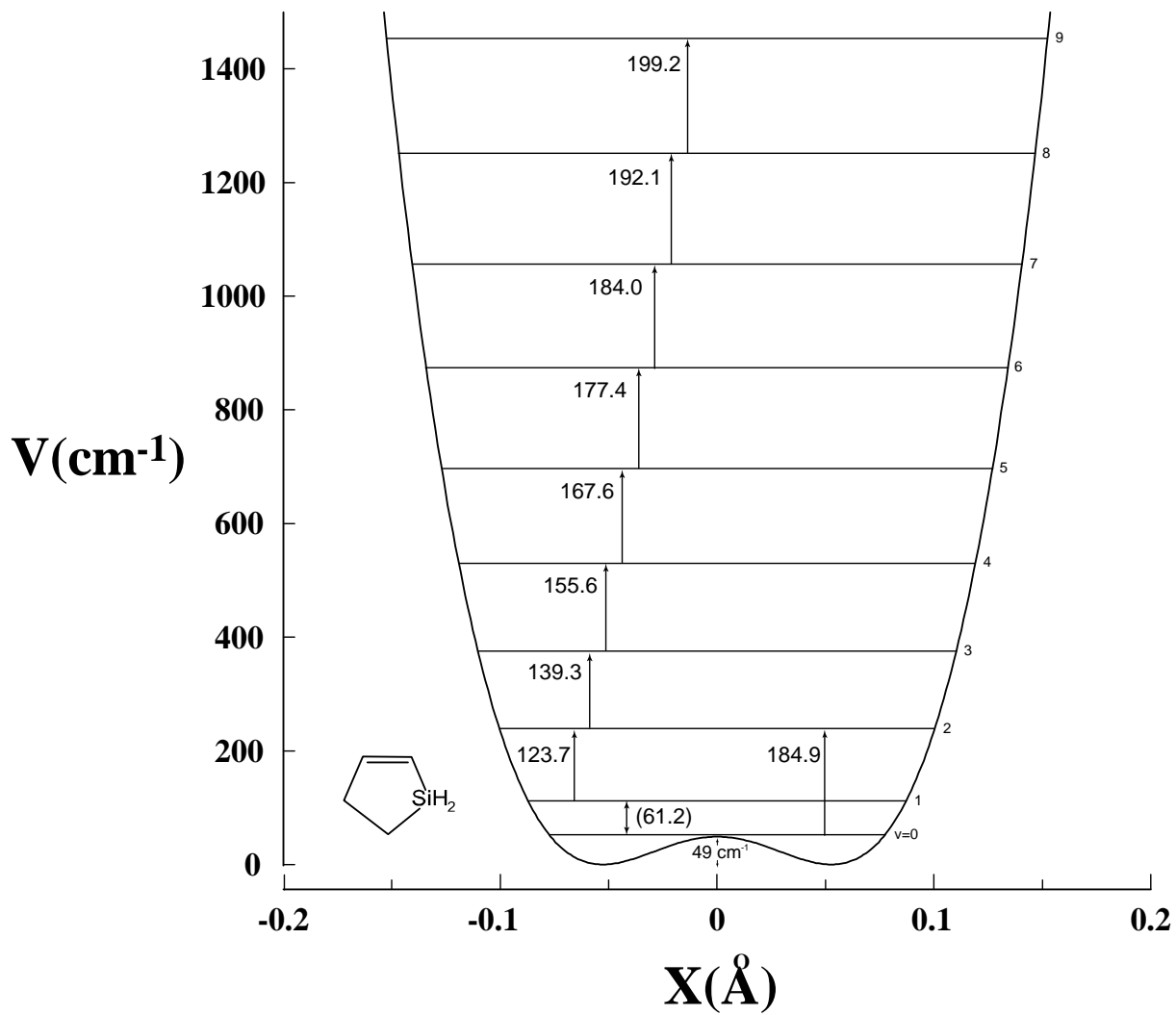


Figure 2.

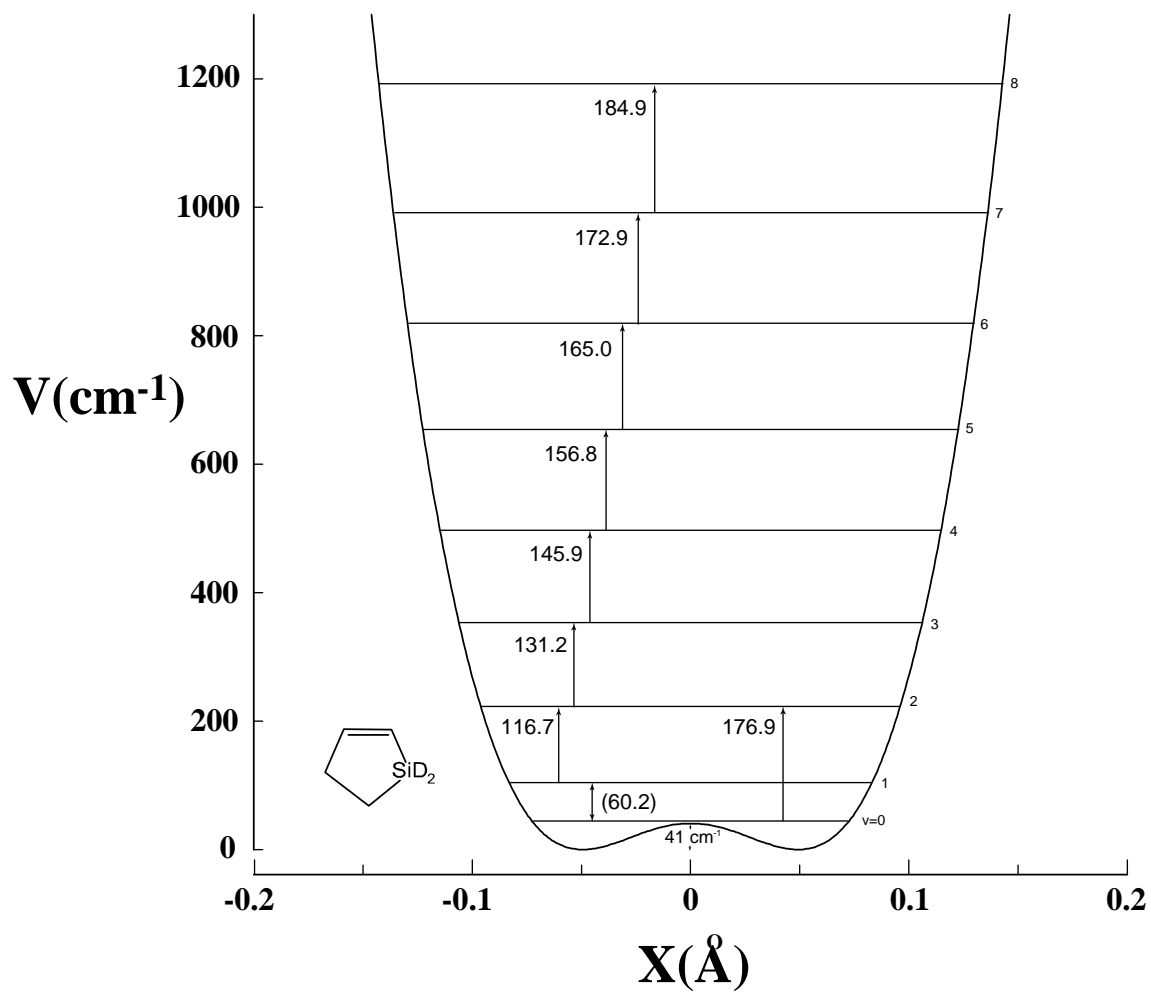


Figure 3.

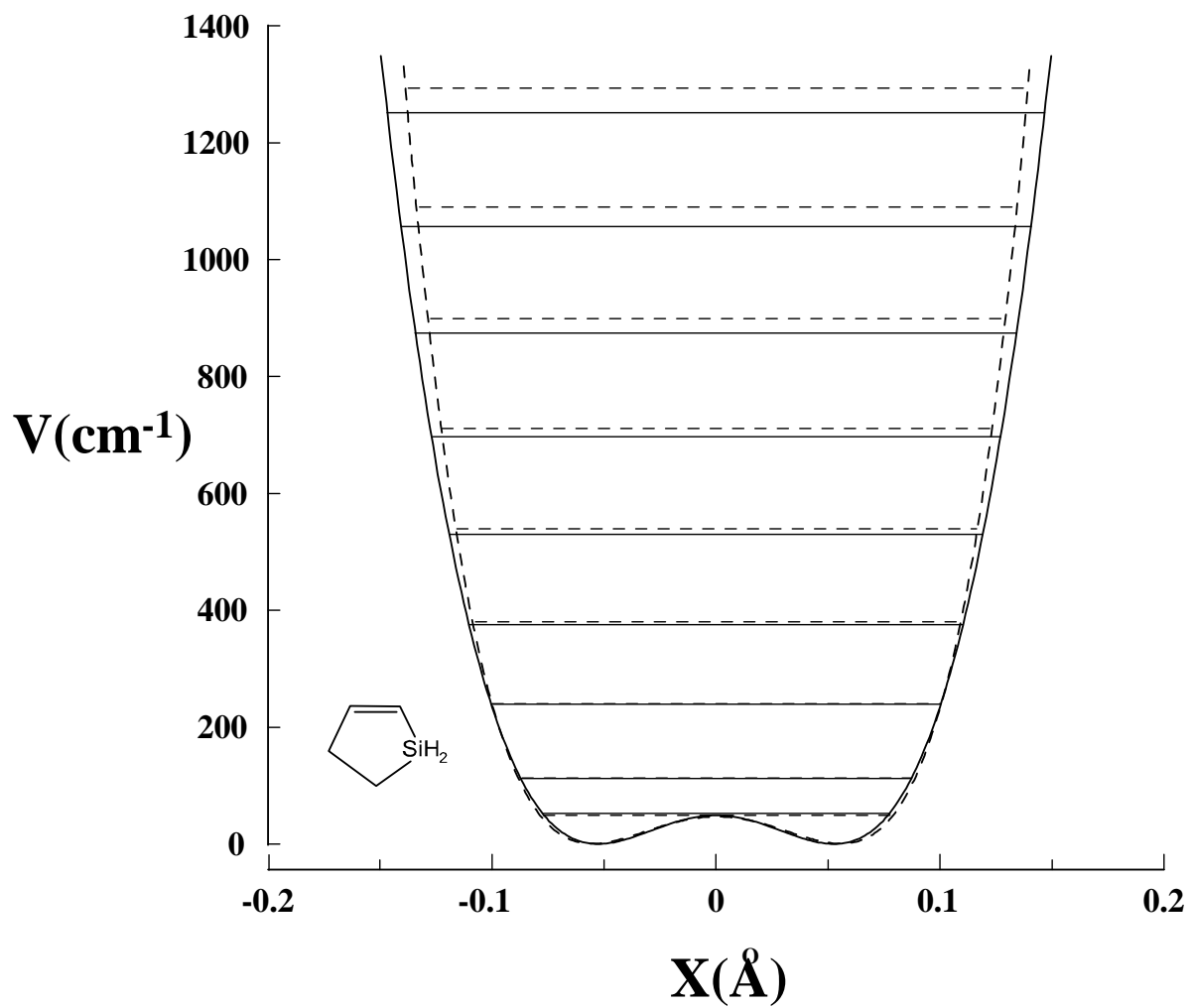


Figure 4.

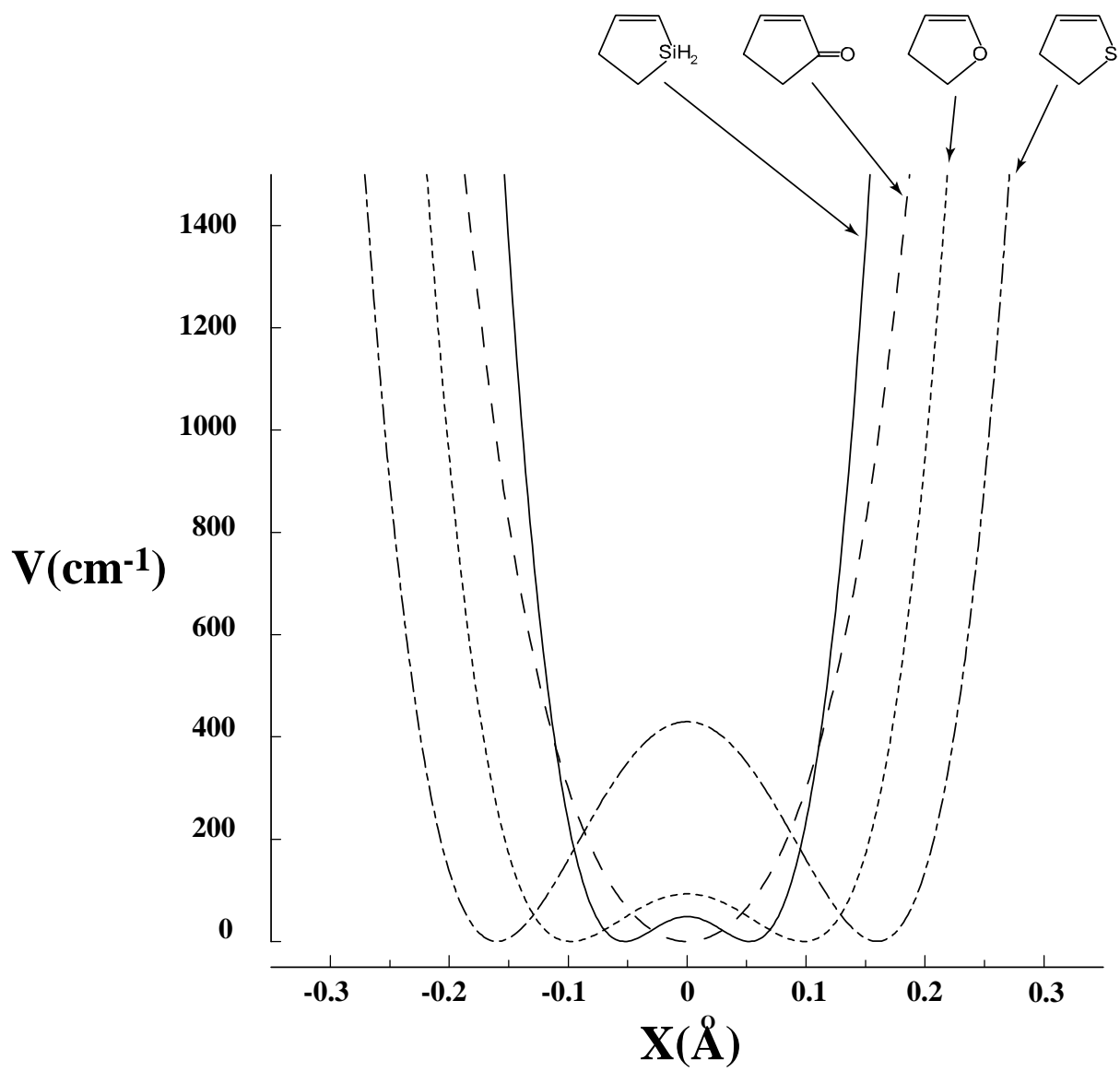


Figure 5.

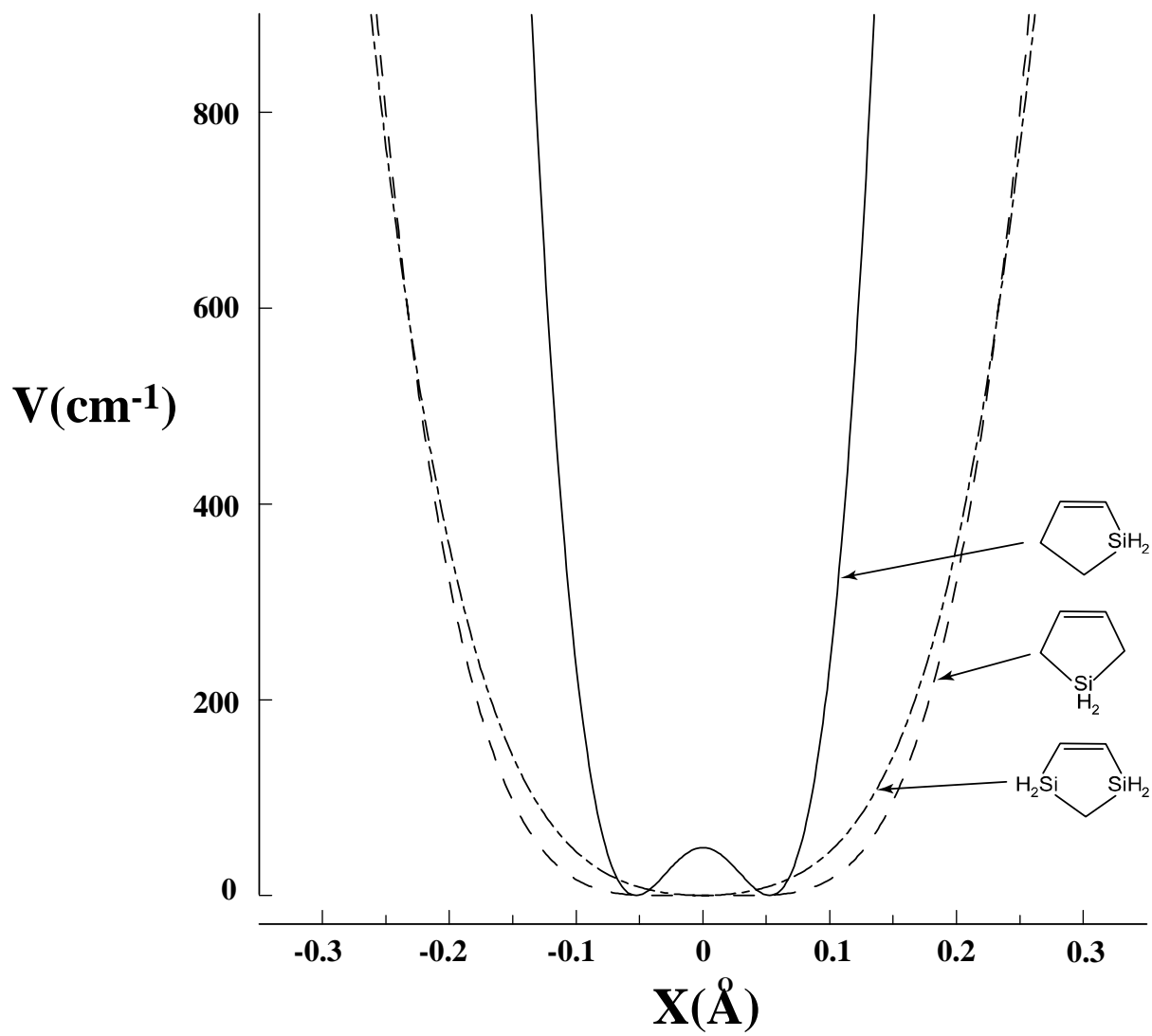


Figure 6.