REGULAR ARTICLE

Fluxional nature in cyclohexane and cyclopentane: spherical conformational landscape model revisited

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Abstract. Spherical conformational landscape model was revisited to include yet another class of cyclic compounds; the derivatives of cyclohexane. The updated model is not only capable of explaining Raman spectral features in fluxional cyclopentane but is also capable of revealing similarities between cyclopentane and cyclohexane derivatives for the first time. At the heart of the model lies the aspect of B/T ring coordinates (B/T conformational platform) that represents different levels of puckering (q). DFT-ωb97xd/6-311 + G* computations confirmed by MP2/aug cc-pVTZ computations were used to fully investigate 16 different derivatives of both cyclohexane and cyclopentane. Intrinsic reaction coordinate, IRC, computations were performed to gain insight into patterned inter-platform pathways connecting ring coordinates. These pathways revealed the coupling strength between bent/boat, B, and twist, T, ring coordinates. The coupling is found to be stronger for cyclopentane compared to cyclohexane. Some spectral features in the overlap region near 1400 cm^{-1} show promising signs on spin–spin relaxation, T_2, mechanism. The work opens up an avenue for conformational studies of medium-sized rings. Also, ongoing studies to unravel potential relationships between conformational flexibility and bioactivity of cyclic compounds are underway.

Keywords. Spherical conformational landscape model; Raman spectral features; fluxional nature; bent/boat(B); twist(T); B/T ring coordinates; spin–spin relaxation (T_2), bioactivity.

1. Introduction

Ring flipping in cyclohexane has been known for many years. The twist and boat conformers, some 5.5–7 kcal/mol less stable, has been proposed to be responsible for the mechanism of ring flipping.[1–11] Cyclopentane with its high gaseous entropy and heat capacity has also been known to have two distinct twists and bent conformations. A dynamic conformational switch in cyclopentane, so-called pseudorotation, has been suggested to explain fluxional nature and diffused line shape in its spectral data.[12–17] However, few attempts have been made to compare these two cyclic molecules and see how the conformational dynamics are related.

A spherical conformational landscape for cyclopentane and its derivatives were proposed in 2016.[18] In that model we classified the 20 conformers into 4 distinct classes and the pseudorotation coordinates into two concentric ring coordinates. The latter include bent (B) and twist (T) coordinates based on the puckering amplitude or q for bent and twist conformers respectively. While the phase φ is defined as free pseudorotation along the circumference of the ring coordinates, we successfully used our model to compare different cyclopentane derivatives and introduced Raman spectral region 1100–1600 cm^{-1} (commonly called D/G band region and referred to as B/T

band region here), as a clear fingerprint for conformational dynamics in cyclopentane and some represented derivatives. Here we try to show how the refined version of spherical conformational landscape works also the exact same way for cyclohexane and potentially other cyclic molecules. Differences between cyclopentane and cyclohexane and their derivatives as well as other cyclic molecules simply lie on a model which reproduce conformational dynamics and their relative stabilities. Further work is underway to look for models that can successfully explain different patterns in Raman spectra for medium-sized rings as well. Many naturally occurring five and six-membered rings are also being investigated to see if Raman spectra and a refined spherical conformational landscape model can predict roots for biological activity and possible insight on drug design based on their conformational properties.

For cyclopentane, previously introduced wheel models,[12] and recent modified versions,[16,17] lacked the idea of separating cast of conformers and their relevant interconversions. For cyclohexane, however, only few studies have addressed the pseudorotation in transition state [19,20] and almost none have explained what it has to do with diffused line shapes. To the best of our knowledge, a first-time pseudorotation model is introduced that can unify the observed and known properties of both cyclopentane and cyclohexane and their derivatives.

2. Computational methods

All computations were done at the DFT-ωb97xd/6-311 + G* level of theory,[21–25] using gaussian g09 package,[26] the reliability of the method was further checked for some conformers at both extremes of stability with MP2/aug cc-pVTZ. The choice for DFT-ωb97xd/6-311 + G* was made due to our previous report on cyclopentane and reliable C-H bond length as well as the geometries obtained. MP2/aug cc-pVTZ, as were the case with cyclopentane, offered very slight changes and huge computational cost for the numerous conformers studied. Computations were done for all conformer of cyclohexane and its many derivatives as well as for all conformers of other new derivatives presented here for cyclopentane. Intrinsic Reaction Coordinate (IRC) computations were performed to gain inside into the coupling strength between bent, B, and twist, T, ring coordinates. The data was used to build the interplay patterns between the two ring coordinates for cyclohexane and its derivatives as well.

3. Results and Discussions

The fluxional nature of cyclopentane is not a unique attribute as previously claimed,[12,16] rather it's a result of the introduced torsion in a twist and bent conformers for cyclohexane and cyclopentane respectively. In cyclohexane, the B/T ring coordinates are not populated that much due to more stable chair conformers that are highly populated in the ground state. However, for cyclopentane, all possible conformers are on the B/T ring coordinates, trapping this beautiful molecule in a constant ultrafast flip flop known as pseudorotation. Deciphering the nature of this populated rovibrational state and its tight relation to Raman spectra (D/G band region) is the main question to be addressed here.

The origin of torsional strain in the cyclic compounds has only appeared in recent literature. Electron momentum distribution EMDs is used to address conformational populations.[27] Cyclopentane has been shown to fulfil a pseudorotational wheel conformation model based on EMD experiments backed up with MD calculations.[28] Aksnes *et al.,* also showed that bi-exponential decay behavior can be observed for cyclohexane spin–spin T_2 relaxation in free versus confined cyclohexane in MCM-41 and similar meso-porous materials.[29–31] In our previous publication, we also showed that freezing can induce such restrictions on cyclopentane pseudorotation and thus sharpen its diffused spectral line shape. The phenomenological model presented here is refined version of the spherical conformational landscape introduced back in 2016, but there are a few very important changes before we discuss the success of the model in explaining the spectral data. The B/T ring coordinates separation is meant to reveal puckering differences is between the conformers (Figure 1). However, the energy difference is small and the puckering difference for B/T coordinates can be traced out in the Raman spectra. The phase φ is believed to be a quantum Brownian motion,[32,33] which serves to minimize the torsional strain along the entire carbonic ring. Two rings are strongly coupled to one another and the coupling can also be clearly seen in the conformational interconversions as represented by the model. Studies on ^{1}H NMR spectra of cyclic compounds are well-documented,[34] and the $^3J_{HH}$ and $^1J_{HH}$ couplings for cyclohexane and cyclopentane have fully been analyzed. However, the C-H charge transfer due to changes in hyperconjugation between B and T conformers, can only be seen in Raman spectral which provide information on carbon hybridization and planarity.
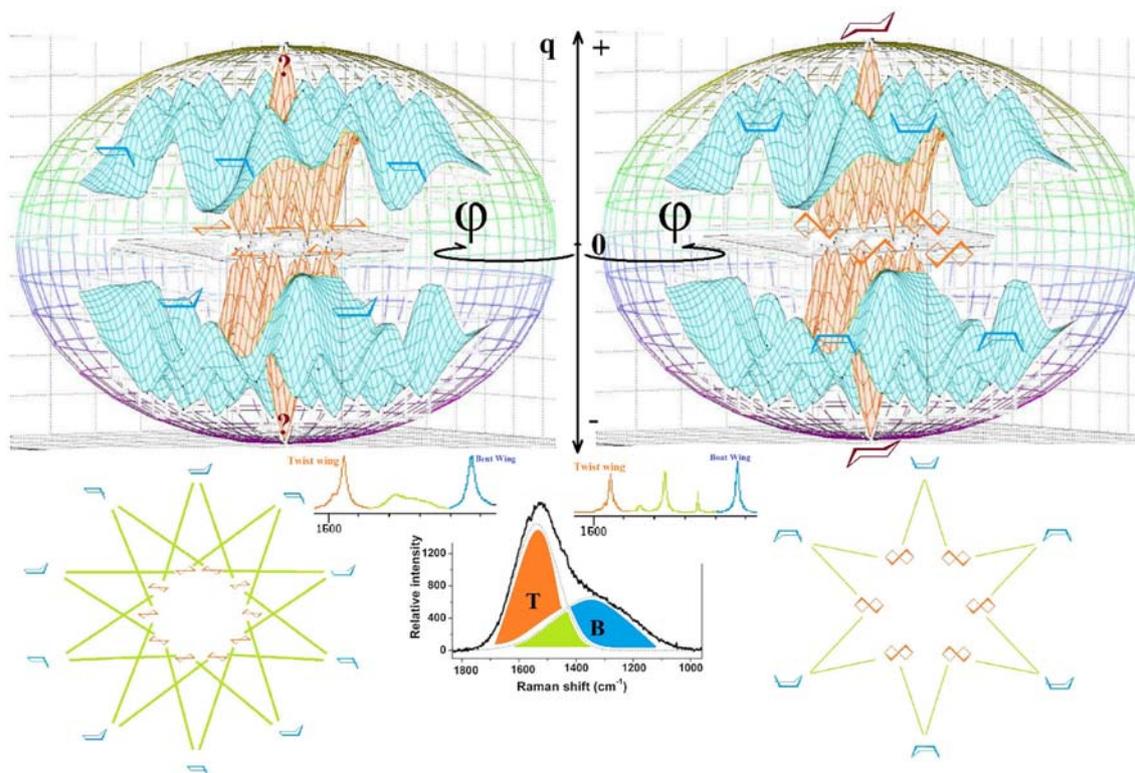
Figure 1. Spherical conformational landscape for cyclohexane vs. cyclopentane (Top). Topical views for Spherical conformational landscape, SCL's, with color codes pertaining to twist wing, bent/boat wing and the overlapping region. (bottom). (Reprinted from our publication[18] with modifications and extensions to include cyclohexane, copyright 2016 Elsevier publishing Co.).

First, the conformational landscape model is presented for both cyclohexane and cyclopentane with some comparisons. First cyclohexane and its derivatives will be considered and then we move to cyclopentane where the fluxional nature is hardly

affected unless in solid-state or with highly restricting substituents. The spherical conformational landscape model is presented in both spherical and topical view in Figure 1 and the most evident difference lies in the lack of any conformers for cyclopentane equivalent to
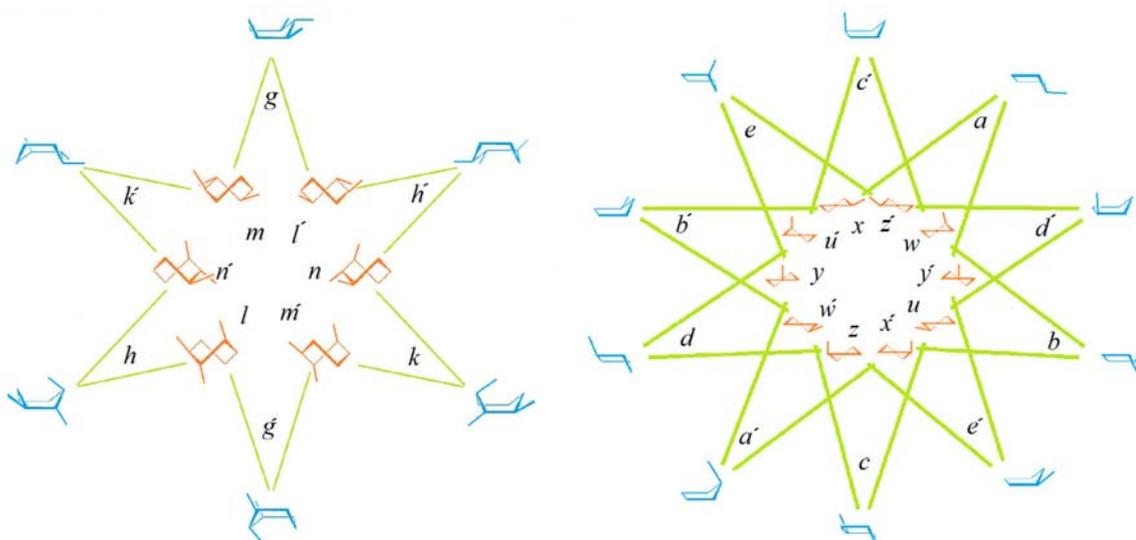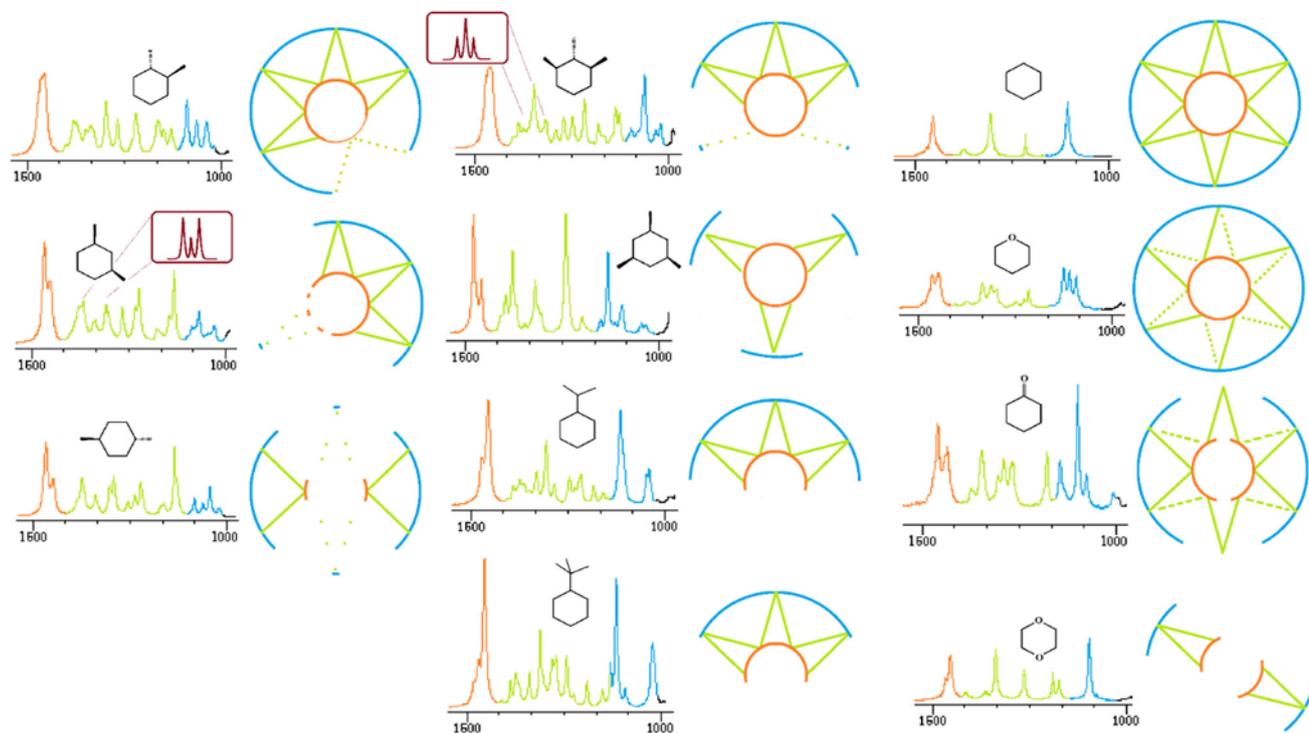

Figure 2. 6-pointed star SCL for 1,2,3 all-trans trimethyl cyclohexane with labelling the conformers along ring coordinates (left). 10-pointed star SCL for methyl cyclopentane with labelling the conformers along ring coordinates (right) (Conformers for all 16 derivatives are numbered according to the schemes shown here).

Table 1. Energies for conformers (as indicated by letters in their SCL's as in Figure 2) of all 10 cyclohexane derivatives. These energies are used to build the connection patterns between B/T ring coordinates in SCL's presented in Figure 3. (Configurations of substituents are given for compounds as cis/trans whereas conformational relations gauch/anti are more reflected in energies as can be seen in Figure 2, where Twist ring conformers become energetically favorable and thus more populated).

Compounds	Conformers/Energies (Kcal/mol)
1,2 trans dimethyl cyclohexane	*l', k'* (7); *n', m, g, h, h', l, n* (8); *m'* (11); *g', k* (14); Chair (0); Flipped chair (3)
1,3 cis dimethyl cyclohexane	*l', m* (8); *k', g, h'* (9); *n, n'* (10); *m', l* (12); Chair (0); Flipped chair (7)
1,4 trans dimethyl cyclohexane	*k, n, h', k', n', h* (5); *m', l, m, l'* (10); *g, g'* (14); Chair (0)
1,2,3 all trans trimethyl cyclohexane	*m, l'* (6); *n', n* (7); *k', h'* (8); *g* (9); *m', l* (10); *h, k* (13); *g'* (18); Chair (0); Flipped chair (5)
1,3,5 all cis trimethyl cyclohexane	*n, l', m, n', l, m'* (7); *g', h', k'* (10); *g, h, k* (16); Chair (0); Flipped chair (9)
Isopropyl cyclohexane	*l, h, n', k', m, g, l'* (6); *g', h'* (10); *n, m'* (14); *k* (19); Chair (0); Flipped chair (6)
t-Butyl cyclohexane	*l, h, n', m, g, l'* (7); *k'* (8); *g', h'* (12); *m', n* (17); *k* (23); Chair (0); Flipped chair (7)
Cyclohexane	*m', n, l', m, n', l* (6); *g', k, h', g, k', h* (7); Chair (0)
Tetrahydropyran	*n, m', n', m* (5); *k, k'* (6); *g', l, h, g, l', h'* (7); Chair (0)
Cyclohexanone	*l', h', n, k, m', l, h, n', k', m* (4); *g, g'* (6); *g, g'* (6); Chair (0)
1,4 Dioxane	*n, k, m', n', k', m* (7); *l', l* (9); *g', h, g, h'* (11); Chair (0)

Table 2. Energies for conformers (as indicated by letters in their SCL's as in Figure 2) of all 6 cyclopentane derivatives. These energies are used to build the connection patterns between B/T ring coordinates in SCL's presented in Figure 4. (Configurations of substituents are given for compounds as cis/trans whereas conformational relations gauch/anti are more reflected in energies as can be seen in Figure 2, where Twist ring conformers become energetically favorable and thus more populated).

Compounds	Conformers/Energies (Kcal/mol)										
Methyl cyclopentane	*a, w, w'* / 0	*e', b'* / 0.5	*z', z* / 1	*y', y, d, c* / 2	*c', d* / 2.5	*u', u* / 3	*b, e, x, x'* / 3.5	*a'* / 4.5			
Cyclopentane	*a, a', b, b', c, c', d, d', e, e'* / 0	*u, u'. w, w', x, x', y, y', z, z'* / 0.2									
Allyl Cyclopentane	*a* / 0	*z', w, d, c, z, w'* / 1	*x, y', e', e, y, x', b, b'* / 2	*u', u* / 4	*c', d'* / 5						
Tetrahydrofuran	*a, d', b, e', c, a', d, b', e, c'* / 0	*u', x, u, x'* / 2	*u', u* / 4	*z', y', z, y* / 5	*w, w'* / 7						
1,3 Dioxolane	*a, b, e', a', b', e* / 0	*u, x', c, d, u', x, c', d'* / 1	*z', y', z, y* / 2	*w, w'* / 10							
1-Methyl cyclopentene	*a', a* / 0	*w, w'* / 22	*u, u'* / 26	*y, y'* / 2	*e* / 3	*d', b', z, x'* / 4	*z', x* / 6	*b, d* / 9	*e'* / 11	*c* / 15	*c'* / 17
Cyclopentanone	*y, y'* / 0	*d, c, c', d'* / 1	*x, z', x', z* / 6	*e, b' e', b* / 8	*a, a'* / 11	*u, u'* / 16	*c'* / 17				

Figure 3. Comparisons of SCL models to 1100–1600 cm^{-1} band in the relevant Raman spectra for 10 different derivatives of cyclohexane. (Note the strong fluxional nature, particularly in twist wing for some derivatives).

stable chair conformers of cyclohexane. This is the reason, why the molecule is in a constant buzz (fluxional) at its ground state. Leutwyler *et al.,* found the strength of external rotation to be 10^{-4} times smaller than the pseudo rotational buzz.[17] Yet the substituent effect can disturb and even in some cases hinder this fluxional nature (as was shown in our previous work).

The model presented here can successfully interpret the observed Raman spectra of almost all different substituents of cyclopentane and cyclohexane. The colors are used to simply emphasize the location of T (in orange) and B (in blue) ring coordinates, while the overlap region is colored in yellowish-green. There is one more subtle change between the model for cyclopentane and cyclohexane and that is the intertwined nature of lines connecting the conformers in two ring coordinates for cyclopentane. This intertwined lines for cyclopentane mean a stronger, hard to be affected, coupling between T and B ring coordinates compared to cyclohexane. This stronger coupling gives the most diffused peak in the overlap region, supported by the fact that all 6 points of the cyclohexane SCL star must be covered to complete a full turn around the ring coordinates, while only 3.33 points of cyclopentane SCL star are enough to cover a full turn around its ring coordinates.

The topical views of SCL for two selected substituents are given in Figure 2, with the conformers labelled around ring coordinates. Tables 1 and 2

provide the energies of all these conformers in cyclohexane and cyclopentane respectively. For all spectral comparisons, a topical SCL is shown which bolds the features of spectra and helps one to compare disturbances in SCL and corresponding Raman spectrum.

As mentioned before, cyclohexane itself does not show a fluxional nature which is also evident in its Raman spectrum (Figure 3, top). However, in some derivatives where one of the chair conformers lies close to boat/twist ring coordinates, this conformational platform becomes easily accessible and the twist ring in, particular, becomes populated (clearly seen as a rise in the intensity of the twist wing peak in the spectrum). For 1,2 trans dimethyl cyclohexane and 1,2,3 all-trans trimethyl cyclohexane, where the twist ring coordinate is energetically favorable along its entire circumference, the twist wing gives a distinctly diffused peak indicating a fluxional nature. It is noteworthy that the main driving force for a populated twist rings are the favorable gauch/anti interactions possible in twist conformers for the above-mentioned structure with certain cis/trans configuration (Figure 2, left panel). This fluxional nature also owes its diffusion to the disrupted boat ring coordinate which further populates the twist ring (Figure 3, top). One can see an increasing split appears in this twist wing when moving from 1,2 trans dimethyl cyclohexane to 1,4 trans dimethyl cyclohexane in the twist rings due to its growing
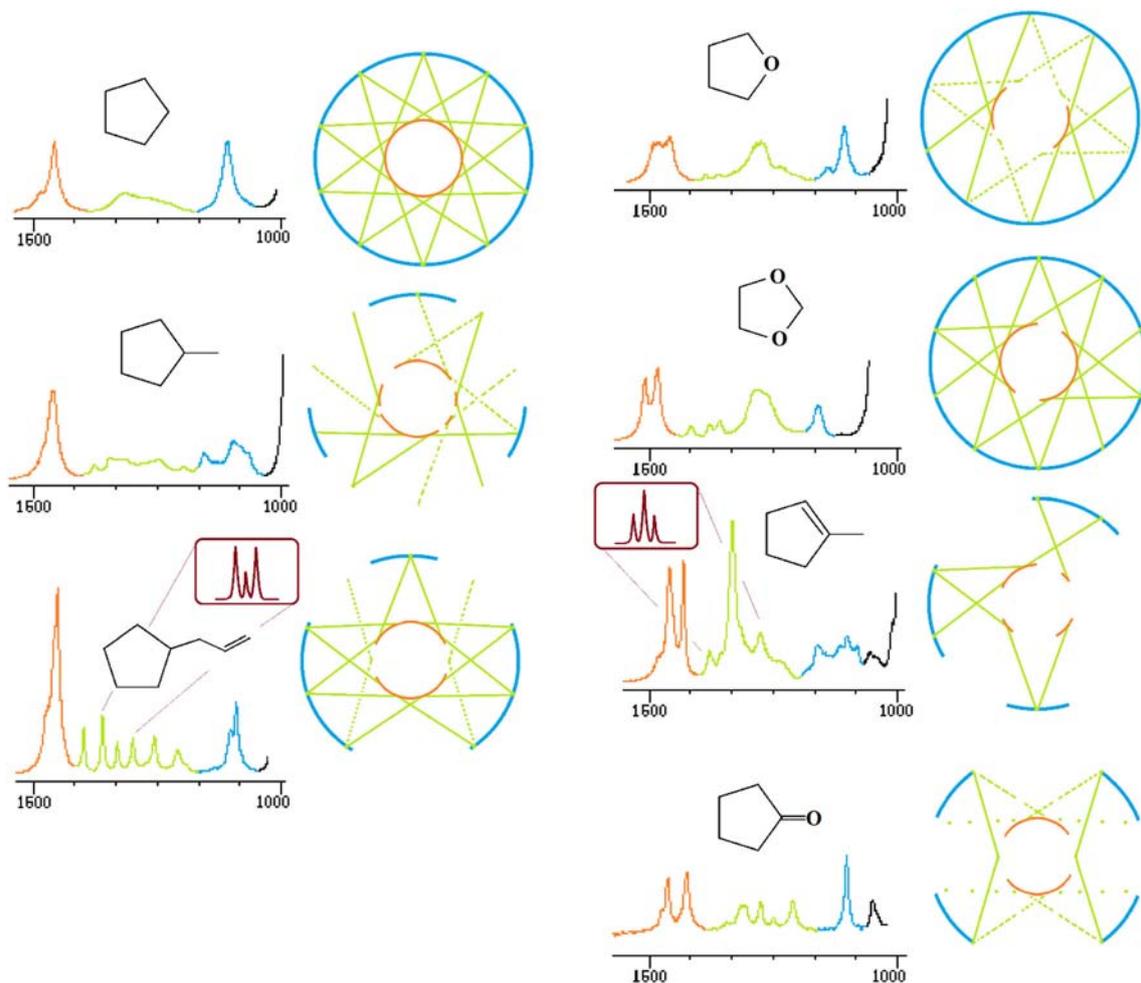
Figure 4. Comparisons of SCL models to 1100–1600 cm^{-1} band in the relevant Raman spectra for 6 different derivatives of cyclopentane.

disruption (Figure 3, left column). Another distinct feature in the Raman spectrum is a triplet peak around 1400 cm^{-1} when three points in the SCL stars are active (Figure 3, middle column). Based on Hubbard diffusion model the shape of these triplets can be classified. Spin–spin T2 relaxations behavior can be analyzed based on these shapes for both cyclohexane and cyclopentane, which will be discussed later. Oxygen bearing Cyclohexane derivatives will range from Tetrahydropyran with the populated twist wing, to cyclohexanone with populated but distinctly split twist wing, to 1,4 Dioxane. The latter clearly shows signs of restricted boat/twist platform that cannot be accessed and populated easily (Figure 3, right column). It is interesting that a restricted B/T platform in 1,4 Dioxane can show a similar spectrum as in Cyclohexane itself. So, while the substituents can switch on the B/T platform through populating twist, they can also severely disrupt B/T platform, thus switching it off.

Cyclopentane is in constant buzz, and in contrast to cyclohexane which can have switched off B/T platform, cyclopentane fluxional nature is hardly affected and can only be frozen in severely restricted cases. Simple alkyl substituents can only disrupt the bent ring coordinate and the overlap region (Figure 4, left column). Oxygen bearing substituents can split the twist wing. This splitting becomes more profound as the bent ring coordinate becomes restricted (Figure 4, right column). A synergic pattern of depleted bent and populated twist conformers is evident for some cyclopentane derivatives, in the B/T platform B/T. Methyl cyclopentane and 1-methyl Cyclopentene apparently demonstrate this feature both in the SCLs and Raman spectra (Figure 4). Severe restriction of cyclopentane pseudorotation happens in some derivatives containing phenyl rings. Such restrictions can also occur upon going to the solid phase, this change accompanies sharpening of the otherwise diffused Raman line shapes (an elaborate discussion of this is discussed in our previous work).

It was mentioned that T$_2$ relaxation for cyclohexane decay in two modes. Here we classify substituents of both cyclopentane, and cyclohexane based on the
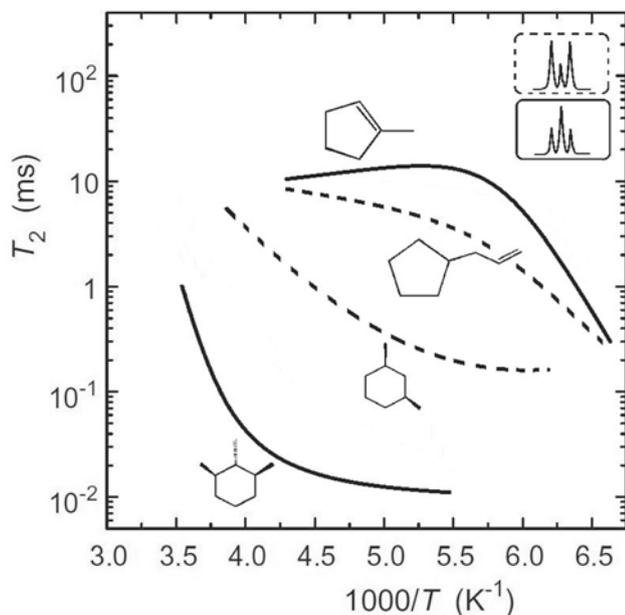
Figure 5. Distinct shapes (given in inlay boxes) of triplet peaks near 1400 cm^{-1} in Raman spectra reveal decay behavior for T2 relaxation based on Hubbard diffusion model. (Biexponential T2 relaxation decays has already been reported for confined cyclohexane in MCM-41 mesoporous materials[29]).

shape of triplets in overlap region to deduce the T2 relaxations and the exponential behavior for such relaxation. Figure 5 illustrates the effect of restriction on biexponential behavior of T2 spin–spin relaxation, in selected substituents for both cyclopentane and cyclohexane. There are ongoing MD computations on this issue to provide more insight on the nature of T_2 relaxation mechanism and its relevance to fluxional dynamics of these molecules.

There is also ongoing research with medical collaborates in a joint effort to unravel any biological activities in compounds containing 5 and 6 membered rings. Fused cyclic compounds like cedorol and its derivatives, form an entire class of bioactive compounds. Conformational studies combined with a clinical search for bioactivity paves a promising path, that will paint the big picture towards a bright future. How does nature exploit such conformational mobilities like fluxional nature to design bioactive molecules? And can this fluxional nature be tailored to funnel desirable dynamics in the biological context? These are the questions to be addressed later.

4.   Conclusions

In this work, we have tried to show that fluxional nature is not unique to cyclopentane, and all cyclic molecules may share a very similar conformational landscape as presented for cyclopentane and cyclohexane as well as their derivatives. Spherical conformational landscape model was refined to include six-membered rings. The B/T platform and its accessibility successfully explained both the differences and similarities between cyclopentane and cyclohexane as well as their derivatives. Many derivatives were studied, and the reliability of the spherical conformational landscape was confirmed by 1100–1600 cm^{-1} band in their Raman spectra while providing new insights on the effect of substituents on the fluxional nature of the B/T platform. Similar modifications of the model are expected to provide far more simple and meaningful conformational platforms for larger cyclic compounds mainly referred to as the medium-sized rings. Classifying conformers into distinct conformational platforms (B/T ring coordinates here) and patterned inter-platform pathways, plays a crucial role to seek out distinct conformational dynamics for medium-sized rings. Such distinct conformational dynamics are expected to be present in 1100–1600 cm^{-1} region of relevant Raman spectra for medium-sized rings. The ability to bold certain dynamical behavior in medium-sized rings, with their numerous conformers, would revolutionize our understanding of their ubiquitous presence in the scaffold of many natural products. Ongoing MD studies on the exact physical origin of fluxional nature would potentially reveal the underpinning dynamics for cyclic molecules and their beautiful chemistry in the near future.

Compliance with ethical standards

References

1. Allinger N L 1964 Conformational analysis in the elementary organic course *J. Chem. Edu.* **41** 70
2. Strauss H L and Pickett H M 1970 Conformational structure, energy, and inversion rates of cyclohexane and some related oxanes *J. Am. Chem. Soc.* **92** 7281
3. Leonard J E, Hammond G S and Simmons H E 1975 Apparent symmetry of cyclohexane *J. Am. Chem. Soc.* **97** 5052
4. Leventis N, Hanna S B and Sotiriou-Leventis C 1997 A three-dimensional energy surface for the conformational inversion of cyclohexane *J. Chem. Edu.* **74** 813
5. Nelson D J and Brammer C N 2010 Toward consistent terminology for cyclohexane conformers in introductory organic chemistry *J. Chem. Edu.* **88** 292
6. Kakhiani K, Lourderaj U, Hu W, Birney D and Hase W L 2009 Cyclohexane Isomerization. Unimolecular

    Dynamics of the Twist-Boat Intermediate *J. Phys. Chem. A* **113** 4570

7. Brügger G, Frey H-M, Steinegger P, Balmer F and Leutwyler S 2011 Accurate determination of the structure of cyclohexane by femtosecond rotational coherence spectroscopy and ab initio calculations *J. Phys. Chem. A* **115** 9567

8. McGrath K J and Weiss R G 1993 Rate of chair-to-chair interconversion of cyclohexane-d12 in its neat plastic crystalline phase *J. Phys. Chem.* **97** 2497

9. Dasgupta S, Tang Y, Moldowan J M, Carlson R M and Goddard III W A 1995 Stabilizing the boat conformation of cyclohexane rings *J. Am. Chem. Soc.* **117** 6532

10. Wiberg K B, Castejon H, Bailey W F and Ochterski J 2000 Conformational studies in the cyclohexane series. 2. Phenylcyclohexane and 1-methyl-1-phenylcyclohexane *J. Org. Chem.* **65** 1181

11. Wiberg K B, Hammer J D, Castejon H, Bailey W F, DeLeon E L and Jarret R M 1999 Conformational studies in the cyclohexane series. 1. Experimental and computational investigation of methyl, ethyl, isopropyl, and tert-butylcyclohexanes *J. Org. Chem.* **64** 2085

12. Lipnick R L 1974 NMR spectroscopy of cyclopentane derivatives. III. Methylcyclopentane *J. Am. Chem. Soc.* **96** 2941

13. Poupko R, Luz Z and Zimmermann H 1982 Pseudorotation in cyclopentane. An experimental determination of the puckering amplitude by NMR in oriented solvents *J. Am. Chem. Soc.* **104** 5307

14. Pitzer K S and Donath W E 1983 Conformations and strain energy of cyclopentane and its derivatives. In: *Molecular Structure and Statistical Thermodynamics: Selected Papers of Kenneth S Pitzer* (World Scientific) pp. 98–103

15. Tomimoto M and Go N 1995 Analytic theory of pseudorotation in five-membered rings. Cyclopentane, tetrahydrofuran, ribose, and deoxyribose *J. Phys. Chem.* **99** 563

16. Ocola E J, Bauman L E and Laane J 2011 Vibrational spectra and structure of cyclopentane and its isotopomers *J. Phys. Chem. A* **115** 6531

17. Kowalewski P, Frey H-M, Infanger D and Leutwyler S 2015 Probing the structure, pseudorotation, and radial vibrations of cyclopentane by femtosecond rotational Raman coherence spectroscopy *J. Phys. Chem. A* **119** 11215

18. Sakhaee N, Jalili S and Darvish F 2016 Spherical conformational landscape shed new lights on fluxional nature of cyclopentane and its derivatives, confirmed by their Raman spectra *Comput. Theor. Chem.* **1090** 193

19. Ross B D and True N S 1983 NMR spectroscopy of cyclohexane. Gas-phase conformational kinetics *J. Am. Chem. Soc.* **105** 4871

20. Offenbach J L, Fredin L and Strauss H L 1981 Vibrational spectra of twist-boat cyclohexane *J. Am. Chem. Soc.* **103** 1001

21. Halgren T A 1996 Merck molecular force field. II. MMFF94 van der Waals and electrostatic parameters for intermolecular interactions *J. Comput. Chem.* **17** 520

22. Cao H-Y, Si D-H, Tang Q, Zheng X-F and Hao C 2016 Electronic structures and solvent effects of unsymmetrical neo-confused porphyrin: DFT and TDDFT–IEFPCM investigations *Comput. Theor. Chem.* **1081** 18

23. Goerigk L and Grimme S 2010 Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals—Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions *J. Chem. Theory Comput.* **7** 291

24. Shao Y, Molnar L F, Jung Y, Kussmann J, Ochsenfeld C, Brown S T, Gilbert A T, Slipchenko L V, Levchenko S V and O'Neill D P 2006 Advances in methods and algorithms in a modern quantum chemistry program package *Phys. Chem. Chem. Phys.* **8** 3172

25. Hratchian H P, Parandekar P V, Raghavachari K, Frisch M J and Vreven T 2008 QM: QM electronic embedding using Mulliken atomic charges: Energies and analytic gradients in an ONIOM framework *J. Chem. Phys.* **128** 034107

26. Frisch M, Trucks G, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B and Petersson G (2009) Gaussian 09, revision a 02, Gaussian. Inc., *Wallingford, CT* **2009** 200

27. Tang Y, Shan X, Niu S, Liu Z, Wang E, Watanabe N, Yamazaki M, Takahashi M and Chen X 2017 Electron momentum spectroscopy investigation of molecular conformations of ethanol considering vibrational effects *J. Phys. Chem. A* **121** 277

28. Dong W, Yang H, Qiu Z and Tang Y 2019 Electron momentum spectroscopy of cyclopentane: A molecular dynamical investigation *J. Electron Spectro. Relat. Phenom.* **230** 40

29. Aksnes D W, Førland K and Stöcker M 2005 1H NMR relaxation and diffusion studies of cyclohexane and cyclopentane confined in MCM-41 *Micropor. Mesopor. Mater.* **77** 79

30. Aliev A E and Harris K D 1997 Dynamic Properties of Cyclohexane Guest Molecules Constrained within the Zeolite H-ZSM-5 Host Structure: A Wide-Line Solid State 2H NMR Investigation *J. Phys. Chem. A* **101** 4541

31. Huang Y and Leech J H 2003 An FT-Raman spectroscopic study of the conformational properties of chlorocyclohexane in zeolites *J. Phys. Chem. B* **107** 7647

32. Quach J Q 2013 Disorder-correlation-frequency-controlled diffusion in the Jaynes-Cummings–Hubbard model *Phys. Rev. A* **88** 053843

33. Dehghani A, Mojaveri B, Shirin S and Faseghandis S A 2016 Parity Deformed Jaynes-Cummings Model: "Robust Maximally Entangled States" *Sci. Rep.* **6** 38069

34. Wu A, Cremer D, Auer A A and Gauss J 2002 Extension of the karplus relationship for NMR spin − spin coupling constants to nonplanar ring systems: pseudorotation of cyclopentane *J. Phys. Chem. A* **106** 657