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A reduced dimensionality model of torsional vibrations in star molecules



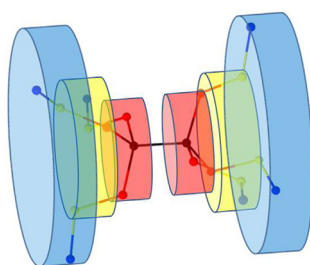
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HIGHLIGHTS

- A reduced dimensionality model is used for torsional vibrations in star molecules.
- The model shows proper asymptotic behavior when extrapolated into the nano-regime.
- Non-bonded torsional interactions are important to the dynamical behavior.
- The model explains the anomalously large apparent inertial moments in these systems.

GRAPHICAL ABSTRACT



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ABSTRACT

The torsional vibrations of star molecules are studied with a reduced dimensionality model. In this model, the molecule is described by two equivalent sets of lumped inertial cylinders and vibrational frequencies are predicted by solution of the coupled equations of motion. Force constants are determined by including them as free parameters in the model and fitting the computed frequencies to their analogs as determined using full normal coordinate analysis at the HFSCF level of theory. Best agreement between the methods occurs when torsional force constants are included for the first *two* layers of the molecule. This reveals that *non*-bonded torsional interactions are important in the vibrational dynamics of these systems. Further insight is afforded by an analysis of why simple harmonic oscillator models are sufficient for modeling some related systems but fail to reproduce the trend in global mode frequencies for saturated aliphatic star molecules. The analysis reveals that the origin of this failure lies in backbone flexibility in these branched polymeric systems.

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1. Introduction

Dendrimers and star molecules are interesting classes of molecules that show promise for application in polymer network scaffolds [1,2] and molecular drug delivery devices [3,4]. Many key materials properties in such systems depend on vibrational motion within the backbone of the dendrimer, and therefore there is interest in understanding these vibrational modes and their

frequencies. In particular, low frequency modes tend to be significantly populated at ambient temperatures. The determination of low frequency vibrational modes is consequently central to understanding the thermal dynamics of a system. For example, Rossi, Scheffler and Blum demonstrated that low frequency vibrational modes dominate the temperature dependent contribution to free energies in polypeptides, and their work suggests that certain protein secondary structural motifs are favored due to presence of low frequency vibrational modes [5]. Other work by Kunal and others shows that the glass transition temperature of polymers is predominantly a function of backbone flexibility [6]. Additionally, Murmu, Adhikari and Wang have applied continuum

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based methods for torsional vibrational frequencies in carbon nanotube–buckyball systems [7].

The traditional technique for studying molecular vibrations is molecular normal coordinate analysis (NCA). It is well established, but becomes intractable for large systems and is therefore impractical for application in the nano-regime. This limitation precludes the application of NCA to dendrimer and star systems, save for the very smallest examples. It is therefore desirable to have a simplified model, both to reduce the dimensionality of the system, as well as to eliminate the need for the costly generation of the Hessian matrix. Toward this end, reduced dimensionality models have previously been reported for polyphenyl chains [8] as well as fullerene superatom dimers [9] and provide new insight into the vibrational dynamics of those systems. Dendrimers and star molecules possess the feature that they can be constructed in a controlled, stepwise manner [10]. Owing to this feature, these molecules are an ideal platform for the study of the properties of dendrimer-based nanomaterials because one may extrapolate into the nano-regime from a systematic progression of smaller systems. Here we capitalize on this feature of star molecules and present a new model to elucidate the nature of torsional oscillations in dendrimers and star molecules.

2. Theoretical methods

2.1. Systems studied

In this study the family of star molecules having the molecular formula $C_{6n+2}H_{12n+6}$ is studied, and for comparison a smaller set of stars with the general formula $C_{6n+2}H_{18}$. Representative molecular structures are shown in Fig. 1. These molecules exhibit a set of torsional vibrations about the axis coincident with the central C–C bond. For each molecule, there exists a low frequency ($< 120 \text{ cm}^{-1}$) global torsional mode (Fig. 2A) and a higher frequency ($\sim 300\text{--}350 \text{ cm}^{-1}$) local torsional mode (Fig. 2B). Molecules larger than molecule B in Fig. 1 also exhibit torsional motion in between these two motions. Additionally, there exist modes in which all atoms in one layer equidistant from the central axis undergo angular motion in opposition to the atoms in the adjacent layer(s) (Fig. 2C). We refer to these types of modes as “barrel” modes.

2.2. Cylinder model

To model the torsional motion of these branched hydrocarbon chains about the principal axis of the molecule, the torsional motion is described as relative rotations among a set of rigid inertias, each constructed to represent a group of main chain carbon atoms equidistant from the principal axis, (hereafter referred to as

“cylinders”). The cylinders are further divided into two sets, one on either side of the plane perpendicular to the principal axis on which the center of mass lies. Hydrogen atoms are not modeled explicitly but instead their masses are lumped together with the carbon atoms to which they are bonded. Thus we arrive at two sets of “nested cylinders,” all with a common axis. A schematic of this is shown in Fig. 3.

We assume a Hooke's Law restoring force about equilibrium angular separation between any two adjacent cylinders. This effectively reduces the number of vibrational normal modes for an n -atom molecule from $3n-6$ to $N-1$, where N is the number of cylinders in the model. For a hydrocarbon that branches out into 3 strands on either side of the center of the molecule, such as those studied in this report, $N = \frac{n-8}{9}$ and this approximation reduces the number of degrees of freedom in the problem by 27-fold. Since normal mode analysis depends on diagonalization of the force constant matrix, which scales as $O(s^3)$ where s is the dimension of the matrix, this dimensional reduction corresponds to a significant decrease in computational cost for large systems. Systems that are intractable to full molecular normal mode analysis can be studied using this cylinder model.

Consider a molecule that has been subdivided into N cylinders. The innermost cylinder pair is defined as cylinders 1L and 1R, (L meaning left and R meaning right.) The next layer of cylinders is named 2L and 2R, and so on until all cylinders have been assigned. The force constant between the i th and $i+1$ th cylinder is denoted k_i and represents the interaction between two adjacent layers on the same half of the molecule. The force constant joining the left and right cylinders of the i th layer is denoted kt_i , representing a torsional restoring force in the i th layer. The angular equations of motion for a molecule of N cylinders are [11]:

$$\begin{aligned} \text{For } i=1 \\ I_{iL} \ddot{\theta}_{iL} &= k_i (\theta_{iL} - \theta_{(i+1)L}) + kt_i (\theta_{iL} - \theta_{iR}) \\ I_{iR} \ddot{\theta}_{iR} &= k_i (\theta_{iR} - \theta_{(i+1)R}) + kt_i (\theta_{iR} - \theta_{iL}) \end{aligned}$$

$$\begin{aligned} \text{For } 1 < i < 2N \\ I_{iL} \ddot{\theta}_{iL} &= k_{i-1} (\theta_{(i-1)L} - \theta_{iL}) + k_i (\theta_{iL} - \theta_{(i+1)L}) + kt_i (\theta_{iL} - \theta_{iR}) \\ I_{iR} \ddot{\theta}_{iR} &= k_{i-1} (\theta_{(i-1)R} - \theta_{iR}) + k_i (\theta_{iR} - \theta_{(i+1)R}) + kt_i (\theta_{iR} - \theta_{iL}) \end{aligned}$$

$$\begin{aligned} \text{For } i=2N \\ I_{iL} \ddot{\theta}_{iL} &= k_{i-1} (\theta_{(i-1)L} - \theta_{iL}) + kt_i (\theta_{iL} - \theta_{iR}) \\ I_{iR} \ddot{\theta}_{iR} &= k_{i-1} (\theta_{(i-1)R} - \theta_{iR}) + kt_i (\theta_{iR} - \theta_{iL}), \end{aligned}$$

where I_{iL} is the moment of inertia of the i th cylinder on the left hand side about the principal axis, θ_{iL} is the angular position of the i th cylinder on the left hand side and the R subscript implies the cylinder on the other side of the molecule. In matrix form, this becomes simply

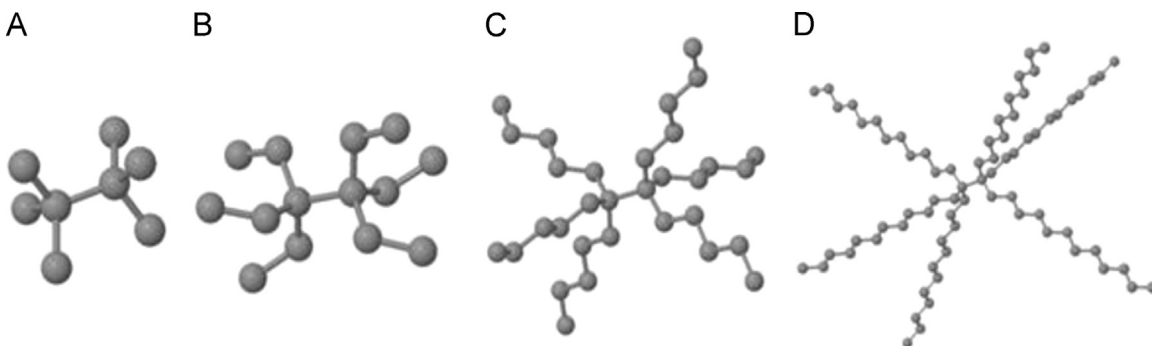


Fig. 1. Representative molecular structures of saturated hydrocarbon star molecules. Hydrogen atoms are omitted for clarity. (A) C_8H_{18} , $N=2$. (B) $C_{14}H_{30}$, $N=4$. (C) $C_{32}H_{66}$, $N=10$. (D) $C_{74}H_{150}$, $N=24$. N is the number of cylinders used to represent the molecule in the model.

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