

Polyyne bending frequencies: why they vary with the square of the harmonic in the infinite limit

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(Received 10 July 2002; revised version accepted 17 September 2002)

The vibrational frequencies of several linear polyynes HC_NH , HC_NI and IC_NI , for even-valued N up to 60, have been obtained using computational quantum chemistry. The bending normal modes have the appearance of classical transverse normal modes of a vibrating string fixed at both ends, for which the frequencies vary with the first power of the harmonic. Our calculations, however, reveal that in the limit of infinite chain length and infinite mass on the ends of the ‘molecular string’, the bending frequencies vary with the square of the harmonic, at all levels of theory. A derivation is presented to explain the discrepancy.

1. Introduction

During a project involving the study of all-*trans* n -alkanes, Hunter and East [1] noticed several vibrational modes that, upon computer animation, had the appearance of normal modes of a classical vibrating string. However, their frequencies did not vary with the first power of the harmonic quantum number n (as string mode frequencies do), but with fractional powers between one and two. Such nonlinear dependence on the harmonic wave number k (k being proportional to n) has been observed before, in the form of computed phonon dispersion curves for transverse modes of both polyyne [2] and polyacetylene [3–5]. We felt it prudent to further investigate this phenomenon, because (a) Brillouin had remarked [6] that the onset of transverse wave frequencies would depend on the first power of k as longitudinal wave frequencies do, (b) the previous phonon dispersion papers (of which we are aware) that demonstrate nonlinear dependence upon k did not explain *why* this is so, and (c) we wished to provide more solid evidence that the dependence does tend specifically towards the square of the harmonic as the polyyne is made to look like a classical vibrating string.

We chose to mimic more closely the classical case of a vibrating string fixed at both ends, by using sets of purely linear polyyne molecules, $\text{X}(-\text{C}\equiv\text{C}-)_k\text{X}$, where the terminal atoms X are hydrogen or iodine atoms. Polyynes are rather unstable molecules, having a penchant for dimerizing and/or forming carbon cages. The synthesis of the iodine-capped versions IC_6I and IC_8I was in fact only reported in the year 2000 [7]. With experimental data unavailable, we logically turned to computational chemistry to determine the approximate bending frequencies.

2. Theoretical methods

The Gaussian 98 software program [8] was used to compute optimized geometries and vibrational harmonic frequencies of normal modes, including the frequencies for molecules with artificially heavy isotopes. The normal modes were animated with the GaussView program [9] on a microcomputer. Three levels of theory were employed: Hartree–Fock self-consistent field (HF-SCF), Møller–Plesset perturbation theory (MP2), and the B3LYP version of density-functional theory [10]. The basis set used for orbitals, dubbed LANL2DZ by Gaussian 98 [8], is a contracted valence double-zeta set, with a single-zeta function for the carbon 1s orbital, and an effective core potential [11] for iodine orbitals up to but excluding 5s and 5p.

Computations were performed on polyyne chains consisting of $N = 8, 14, 20, 40$ and 60 carbons. Terminal atoms were chosen to be ^1H , ^{127}I , ^{500}I , ^{999}I and $^{1\text{N}^{\text{F}}}\text{I}$, with the isotope mass (in amu) listed as the pre-superscript, and $^{1\text{N}^{\text{F}}}\text{I}$ referring to an iodine mass of 10^{17} (99 999 999 999 999 999) amu. HF calculations were executed for all lengths of polyynes, whereas the MP2 calculations were completed only for $N = 8$, and the B3LYP calculations were employed only for $N = 8$ and 14. Animations of the $N/2$ lowest-frequency (doubly degenerate) bending vibrations of each molecule all resembled quite nicely the standing waves of a string. There were in fact N doubly degenerate bending modes for each molecule, but the ones beyond $N/2$ did not look as smooth as the others because of the discretized nature of the molecular string. The residual noise in the normal mode diagonalization, as measured by the size of the ‘zero eigenvalues’ for rotation and translation, was less than 0.2 cm^{-1} for our longest molecules.

3. Results

For each molecule and each level of theory, the bending frequencies were identified via animation of the normal modes, and a plot of these frequencies ν_n versus harmonic n was made. Figure 1 shows the three general shapes seen in these graphs. Each point represents two transverse modes, vibrating in directions perpendicular to each other and to the molecular axis. This plot can be seen to be equivalent to phonon dispersion plots of ν versus k by noting that the frequencies above 450 cm^{-1} correspond to ‘optical’ modes, while the frequencies below 450 cm^{-1} correspond to ‘acoustic’ modes. For a polyyne of N carbon atoms, the optical and acoustic branches have roughly $N/2$ normal modes each in the first Brillouin zone. The final points above 850 cm^{-1} appear much higher than all the others as they represent nearly pure hydrogen bending modes.

In figure 1, the first few frequencies are seen to vary in a power-law relationship with the harmonic, that is $\nu_n = cn^p$. The power-law relationship fails for the higher harmonics, however, because the discretization of the string is not fine enough to model these string-like modes appropriately, and hence we had to restrict ourselves to considering only those harmonics that are modelled well, that is those that will obey a power-law relationship.

To fit a power law to each frequency-versus-harmonic plot, four different choices of data truncations were tested: (1) the first $N/2$ harmonics; (2) the first $N/4$ harmonics; (3) the first three harmonics; (4) a varying

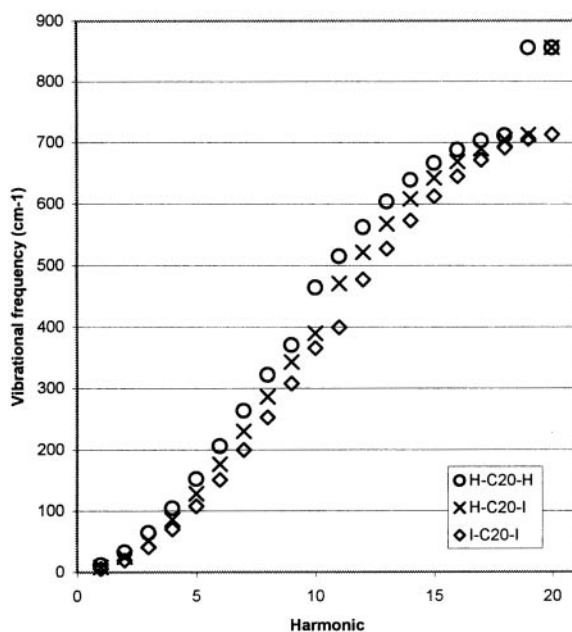


Figure 1. Vibrational frequencies (HF-SCF) for transverse bending modes of polyynes, as a function of string harmonic.

number of harmonics depending on the number of iodine ends present in the molecule ($N/2$ for IC_NI , $N/2 - 1$ for HC_NI , and $N/2 - 2$ for HC_NH). It was found that the first $N/4$ harmonics resulted in the most accurate fits, and therefore this choice for truncation was used exclusively.

The resulting powers fell between 1 and 2, and were dependent on the mass of terminal atoms, length of chain, and level of theory. Figure 2 shows their dependence upon the mass of terminal atoms, for the HC_{60}X and XC_{60}X molecules at the HF-SCF level of theory. Figure 3 shows their dependence upon the length of chain, for molecules with one or two ^{127}I termini, at the HF-SCF level of theory. Both figures suggest that the power p might be 2 in the limit of fixed ends and uniform string density (the so-called ‘infinite limit’). Table 1 presents the results from MP2 and B3LYP, which could only be done on smaller polyynes, and the same trend towards $p=2$ in the infinite limit is suggested. Figure 4 plots the powers from HF-SCF data for symmetrically capped molecules, as functions of both chain length and mass of termini, and in this plot the trend towards a power of two in the infinite limit is clearly seen.

4. Discussion

4.1. Traditional vibrating string solution

To demonstrate why the power tends towards a value of two, we will first recite the common textbook results for the standing modes of a vibrating string fixed at both ends. They obey the differential equation

$$\frac{\partial^2 y(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y(x, t)}{\partial t^2} \quad (1)$$

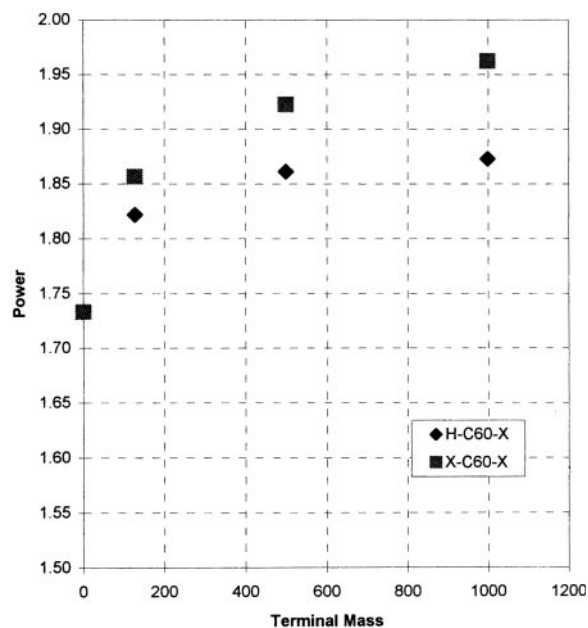


Figure 2. Power-law exponent versus terminal mass.

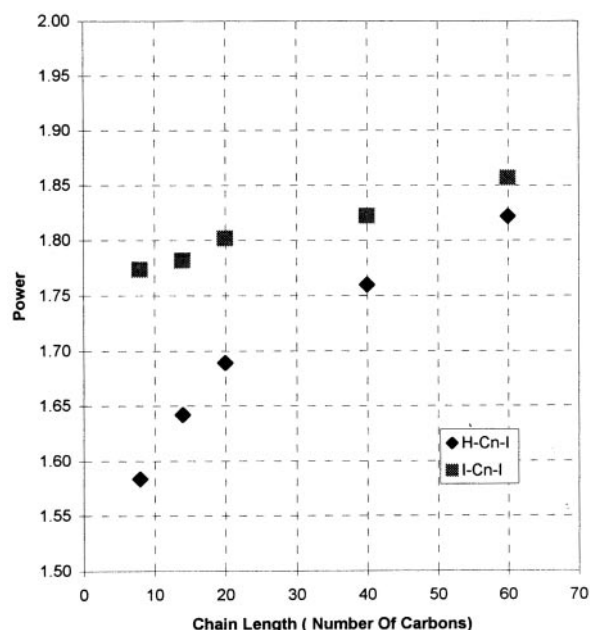


Figure 3. Power-law exponent versus length of polyyne.

Table 1. Power-law exponents: effect of the level of electronic structure theory employed for the frequencies.

	HF-SCF	B3LYP	MP2
IC ₁₄ I	1.78	1.90	—
IC ₈ I	1.77	1.86	1.77
HC ₁₄ H	1.50	1.48	—
HC ₈ H	1.37	1.35	1.33

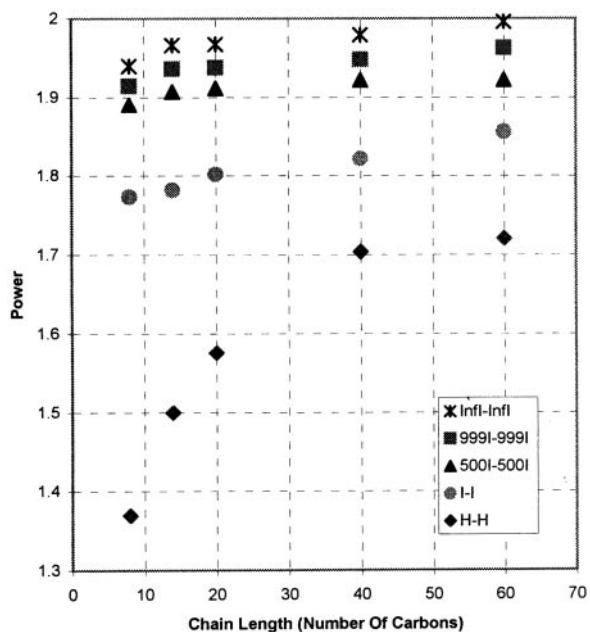


Figure 4. Power-law exponent versus terminal mass and length of polyyne. This plot contains all of our HF-SCF-based results for symmetrically capped polyynes.

where $y(x,t)$ is the vertical displacement of the horizontally pinned string, at horizontal position x and at time t , and v is the velocity of the wave. For the boundary conditions $y(0,t) = y(L,t) = 0$, the solutions are

$$y_n(x,t) = A \cos\left(\frac{n\pi v}{L}t\right) \sin\left(\frac{n\pi}{L}x\right), \quad n = 1, 2, 3, \dots, \quad (2)$$

where n is the quantum number for the harmonic, A is the amplitude of the wave, and L is the length of the string. The frequency ν_n of the oscillating string is found by setting

$$2\pi = \frac{n\pi v}{L} (v_n^{-1}),$$

resulting in

$$\nu_n = \frac{nv}{2L}. \quad (3)$$

Why, then, do polyyne bending frequencies vary with n^2 in the infinite limit? The problem lies in the assumptions behind the velocity v of the wave, normally given as

$$v = \left(\frac{T}{\rho}\right)^{1/2} = \left(\frac{LT}{M}\right)^{1/2} \quad (4)$$

where ρ is the (uniform) mass density M/L of the string, and T is the tension in the string owing to initial stretching of the string. In the polyyne bending case, the mass density does approach uniformity in the infinite limit, but the initial tension is zero! There is instead a time-dependent tension, created by the time-dependent elongation ΔL of the string during vibration. This time-dependent tension is ignored in textbook presentations, because it is assumed to be much smaller than the initial tension.

4.2. Generalization of the tension T

Let the restoring force (the time-dependent tension) be proportional to the elongation ΔL via Hooke's law. If the tension and the length of the string at rest are T_0 and L_0 , respectively, then $L = L_0 + \Delta L$ and $T = T_0 + k\Delta L$. The expression for the velocity of the wave becomes

$$v = M^{-1/2} (L_0 T_0 + [T_0 + kL_0][\Delta L] + k[\Delta L]^2)^{1/2} \quad (5)$$

which is now time-dependent. This alters the governing differential equation (1), making it much more complicated to solve. We shall make the assumption that the substitution of the *time-averaged* velocity \bar{v} for v in equations (1)–(3) is a reasonable approximation.

The expression for ΔL is found by considering L to be the length of a curved line, which from calculus is

$$L = \int_0^{L_0} \left[1 + \left(\frac{\partial y}{\partial x} \right)^2 \right]^{1/2} dx,$$

therefore

$$L = \int_0^{L_0} \left[1 + \left(\frac{An\pi}{L_0} \right)^2 \cos^2 \left(\frac{n\pi\bar{v}}{L_0} t \right) \cos^2 \left(\frac{n\pi}{L_0} x \right) \right]^{1/2} dx.$$

We simplify the integral by defining $\lambda = A/L_0$ and assuming $\lambda \ll 1$, that is, the amplitude of the vibration is much smaller than the length of the string. Then, using the Taylor series approximation $(1+x)^{1/2} \approx 1 + x/2$ for small x , the integral becomes

$$L = \int_0^{L_0} 1 dx + \int_0^{L_0} \frac{1}{2} (\lambda n\pi)^2 \cos^2 \left(\frac{n\pi\bar{v}}{L_0} t \right) \cos^2 \left(\frac{n\pi}{L_0} x \right) dx, \quad (6)$$

$$L = L_0 + L_0 \frac{(\lambda n\pi)^2}{4} \cos^2 \left(\frac{n\pi\bar{v}}{L_0} t \right), \quad (6)$$

therefore

$$\Delta L = L_0 \frac{(\lambda n\pi)^2}{4} \cos^2 \left(\frac{n\pi\bar{v}}{L_0} t \right). \quad (7)$$

Hence the generalized expressions for tension and wave velocity are

$$T = T_0 + kL_0 \frac{(\lambda n\pi)^2}{4} \cos^2 \left(\frac{n\pi\bar{v}}{L_0} t \right), \quad (8)$$

$$v = M^{-1/2} \left\{ L_0 T_0 + [T_0 + kL_0] \left[L_0 \frac{(\lambda n\pi)^2}{4} \cos^2 \left(\frac{n\pi\bar{v}}{L_0} t \right) \right] + kL_0^2 \frac{(\lambda n\pi)^4}{16} \cos^4 \left(\frac{n\pi\bar{v}}{L_0} t \right) \right\}^{1/2} \quad (9)$$

and the time-averaged wave velocity would be obtained by integrating over one period

$$P = 2L_0/n\bar{v},$$

that is

$$\bar{v} = \frac{1}{P} \int_0^P v dt. \quad (10)$$

4.3. In the limit of zero initial tension

In our particular case where $T_0 = 0$, the velocity from equation (9) becomes

$$v = M^{-1/2} \left\{ kL_0^2 \frac{(\lambda n\pi)^2}{4} \cos^2 \left(\frac{n\pi\bar{v}}{L_0} t \right) + kL_0^2 \frac{(\lambda n\pi)^4}{16} \cos^4 \left(\frac{n\pi\bar{v}}{L_0} t \right) \right\}^{1/2}. \quad (11)$$

If we ignore terms higher than first order in λ , we obtain

$$v = L_0 \left(\frac{k}{M} \right)^{1/2} \frac{\lambda n\pi}{2} \left| \cos \left(\frac{n\pi\bar{v}}{L_0} t \right) \right|. \quad (12)$$

The time-averaged velocity is then

$$\bar{v} = \frac{1}{P} \int_0^P L_0 \left(\frac{k}{M} \right)^{1/2} \frac{\lambda n\pi}{2} \left| \cos \left(\frac{n\pi\bar{v}}{L_0} t \right) \right| dt,$$

$$\bar{v} = \frac{n\bar{v}}{2L_0} L_0 \left(\frac{k}{M} \right)^{1/2} \frac{\lambda n\pi}{2} 4 \int_0^{P/4} \cos \left(\frac{2\pi t}{P} \right) dt,$$

$$\bar{v} = n^2 \bar{v} \left(\frac{k}{M} \right)^{1/2} \lambda \pi \left[\frac{L_0}{\pi n \bar{v}} \right],$$

$$\bar{v} = \lambda n L_0 \left(\frac{k}{M} \right)^{1/2}. \quad (13)$$

Plugging this into equation (3) for the vibrational frequency gives

$$v_n = \frac{\lambda n^2}{2} \left(\frac{k}{M} \right)^{1/2}. \quad (14)$$

Hence, the bending frequencies for a string with zero initial tension should vary not with n , but with n^2 . This explains our findings based on computed frequencies for polyynes of long length and heavy terminal atoms. The extra power of n arose from the time-dependent tension created by the small elongation of the molecular string upon bending, which is neglected in usual treatments of classical vibrating strings.

4.4. Connection with one-dimensional-lattice phonon theory

We redid the derivation in the style Brillouin used to demonstrate linear dependence versus harmonic wave number k for longitudinal modes [6]. The derivation is longer than the one above, but we again obtained dependence on the square for the first few harmonics. We suspect that Brillouin's forecast of linear dependence may have arisen from assuming that the one-dimensional lattice exists in a three-dimensional crystal,

and hence that the forces due to atoms from neighbouring chains are exerting forces as well. This would indeed contribute linear terms to the expression for transverse frequencies.

5. Conclusions

Computational predictions of the polyynes chain bending vibrations using HF-SCF, B3LYP, and MP2 levels of theory revealed that relationships exist between the bending (transverse) vibrational frequencies and (a) the length of the chain, (b) the mass of the terminal atoms, and (c) the harmonic of the vibration. Extrapolation and combination of the first two relations shows that when the chain is of infinite length and has terminal atoms of infinite weight at the ends, the third relation will be that frequency is proportional to the square of the harmonic quantum number n . This is unlike the frequencies of the transverse modes of a classical vibrating string fixed at both ends, which are proportional to the first power of n . This result can be explained by recognizing that the problem is similar to the classical case of a stretched, vibrating string fixed at both ends, except that the initial tension T is zero and must be replaced by a small, time-dependent tension created by the vibration itself. Observed powers of less than 2 for particular polyynes are due to the non-uniformity and discretization of the string, and the use of terminal atoms of non-infinite mass.

Drs. Nader Mobed, Richard Barton, and Gary Diver (University of Regina) as well as an anonymous referee are thanked for related discussions.

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