Electronic structure and properties of strained polymers: 1. Methods for polyethylene

James R. Shoemaker, Thomas Horn and Peter D. Haaland*
Air Force Institute of Technology, Wright-Patterson Air Force Base, OH 45433, USA

and Ruth Pachter and W. Wade Adams
Wright Laboratory, Materials Directorate, WL/MLPJ, Wright-Patterson Air Force Base, OH 45433, USA
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The modulus and strain-dependent frequency spectrum of polyethylene have been computed from a cluster of C_6H_{12} units using the semi-empirical AM1 Hamiltonian and unrestricted Hartree–Fock wavefunctions. The computed modulus substantially exceeds experimental values, a result which derives from neglect of electron correlation in the calculations. Good qualitative and quantitive agreement with reported strain-dependent frequencies is found, suggesting that the method describes cubic anharmonicity in the bonding while systematically overestimating components of the Hessian.

(Keywords: polyethylene; structure; electrons)

INTRODUCTION

Semi-empirical molecular orbital methods have proven useful for describing the thermochemical properties of large molecules. These methods solve the Hartree–Fock equations using parameterized forms of the two-electron coulomb and exchange integrals which are generated from empirical data such as ionization potentials, heats of formation, dipole moments and equilibrium geometries[1]. In this report we probe the utility of one such molecular orbital method using the Austin Model 1 (AM1) Hamiltonian[2], for describing the microscopic behaviour of strained polymers.

The quantum mechanics of polymers can be approached from either a solid-state or molecular point of view[3]. The former, with periodic boundary conditions and the ansatz of Bloch orbitals, leads naturally to the **k**-dependent optical and electronic properties. However, a clear definition of the crystal's energetics requires computation at an unbiased ensemble of **k** points in the first Brillouin zone[4]. The latter forms a cluster from a molecular fragment whose ends are mathematically wrapped together[5]. In polymer systems where intrachain interactions are more important than those between chains, the cluster model provides thermodynamic insight with more modest computational requirements[6].

The second paper in this series, which concentrates on the calculation of polymer modulus, finds the calculated moduli of infinite chains to substantially exceed the measured tensile moduli of three-dimensional crystals[7,8]. One explanation for this overestimate relies on the reduction of measured moduli by morphological defects. However, the fact that semi-empirical methods in general, at the AM1 level in particular, are parameterized using equilibrium experimental data suggests that one may encounter systematic errors when exploring structures which are far from their equilibrium conformation.

In this paper we examine computed and experimental estimates of tensile moduli and strain-dependent vibrational frequencies in polyethylene. The choice of polyethylene for comparison of experiment and theory is motivated by the quality and quantity of experimental data available for this system and the relatively well-defined morphology of the samples on which experiments were performed. In addition to the polymer calculations, the equilibrium structure and vibrational frequencies for the polyethylene oligomer hexane in a planar zig-zag conformation were explored with semi-empirical and *ab initio* calculations. The objective of this comparison is to provide insight into systematic errors in the AM1 force field which result from a neglect of electron correlation.

METHOD

Electronic structure calculations were performed with MOPAC version 5.0 using the AM1 Hamiltonian and unrestricted Hartree–Fock (UHF) wave-functions on a Silicon Graphics 4D/220 workstation. Cluster geometries were optimized without geometric constraints to generate equilibrium conformations and energies. The number of CH_2 units in the cluster was varied to ensure that the models did not display end effects or a cluster-size-dependent heat of formation (*Table 1*). Constrained optimizations were then performed fixing only the length along the strain (c) axis. The enthalpies of these structures compared to that of the equilibrium structure

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*To whom correspondence should be addressed

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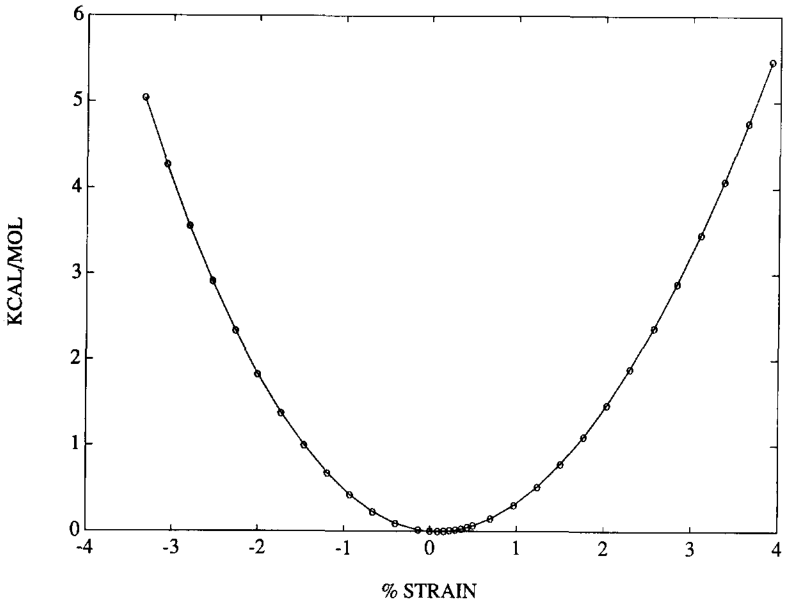

Figure 1 Change in enthalpy (kcal mol^{-1}) for the C_6H_{12} cluster *versus* strain computed with the AM1 Hamiltonian (○). A cubic polynomial fit to the computed energies (—) yields a second derivative of 72.4 kcal (mol $Å^2)^{-1}$ and a modulus of 407 GPa

Table 1 Variation of calculated geometric parameters and enthalpy of formation, ΔH_f, with the number of CH_2 units in the unit cell, n, calculated with the AM1 Hamiltonian

n	C–C (Å)	∠CCC (°)	C–H (Å)	$\Delta H_f/n$ (kcal mol^{-1})	Modulus (GPA)
4	1.514	110.00	1.121	−5.25	403
6	1.513	111.11	1.121	−6.48	407
8	1.513	111.21	1.122	−6.79	411
10	1.513	111.22	1.122	−6.83	411

Table 2 Geometric parameters for planar zig-zag n-hexane using MOPAC/AM1, Gaussian 90 UMP2/g-31g, electron diffraction of gaseous alkanes and X-ray crystallography of $C_{36}H_{74}$

	C–C (Å)	∠CCC (°)	C–H (Å)	Ref.
AM1	1.514	110.00	1.122	
MP2	1.544	113.2±0.4	1.121	
Diffraction	1.531	112.9±0.2	1.118±0.006	13
X-ray	1.534±0.006	112.02±0.35		14

were used to form a plot of the restoring enthalpy associated with uniform strain (*Figure 1*). The second derivative of this restoring enthalpy at equilibrium, $d^2H/d\Delta^2$, is related to Young's modulus ε:

$$\varepsilon = \frac{l}{\sigma}\frac{d^2H}{d\Delta^2}$$

where σ, l and Δ are the cross-sectional area, chain length and strain, respectively. Use of the enthalpy H rather than the free energy F is justified if the second derivatives of entropy and volume with respect to strain are small compared to $d^2H/d\Delta^2$. This condition is satisfied in the limit of small strain, where Young's modulus is defined. The cross-sectional area σ is taken from the crystal structure[9] and assumed to be independent of strain (Poisson's ratio is assumed to be zero). The chain length l is that computed from the equilibrium geometry.

The size of the repeat unit in the cluster calculation was increased until extensive geometric and thermodynamic properties were obtained. The single-chain polyethylene properties were examined using a cluster of C_6H_{12} units. The equilibrium length of this cluster was 7.49 Å and the corresponding heat of formation was −38.91 kcal mol^{-1}. The computed bond lengths and angles were equal to experimental values within the standard error reported for the AM1 Hamiltonian (*Table 2*).

Structures obtained in the constrained optimization were then used to compute a spectrum of vibrational frequencies at each strain. This involves computing and diagonalizing the semi-empirical Hessian:

$$\mathscr{H}_{ij} = d^2H/dx_i dx_j$$

to obtain vibrational frequencies and normal modes. Use of the six-carbon cluster complicates comparison of the computed frequencies with experimental values obtained from crystalline polymers. The line group of the chain is D_{2h}, which coincidentally is isomorphic to the factor group of the polyethylene crystal[10]. This gives rise to $3N - 4 = 50$ vibrational modes, Γ_{vib}, which transform as:

$$\Gamma_{vib} = 9A_g + 8B_{1g} + 6B_{2g} + 3B_{3g} + 3A_u + 5B_{1u} + 8B_{2u} + 8B_{3u}$$

The four remaining modes correspond to translation and rotation about the c-axis. The use of three crystallographic units in the cluster mixes contributions from $\mathbf{k} = (0, 0, \frac{1}{3})$ into the resulting frequency spectrum, further complicating assignment of vibrational modes.

Calculations on the planar zig-zag conformation of the hexane oligomer were performed with the MOPAC/AM1 method and with *ab initio* techniques which include electron correlation. The optimized geometry and frequency spectrum were examined at the MP2/6-31g level of theory with Gaussian90[11]. The geometry changes with addition of polarization functions to carbon (UMP2/6-31g*) using CADPAC[12] were small, and frequency calculations at this level were precluded by computer memory limitations.

RESULTS

The calculated geometries for polyethylene and hexane are as expected for the AM1 Hamiltonian. Average errors in bond length of 0.05 Å and bond angle of 3.3° for isolated molecules have been reported for over 600 compounds[1]. The computed bond lengths and angles for polyethylene and hexane agree with the experimental values obtained by electron diffraction of gaseous alkanes[13] and by X-ray crystallography[14] of $C_{36}H_{74}$ (*Table 2*). The differences between geometries computed using AM1 and MP2/6-31g are subtle, and are in substantial agreement with more elaborate calculations[15].

The change in enthalpy with strain along the c-axis for the polyethylene cluster is shown in *Figure 1*. The Young's modulus computed from the second derivative of this curve ($d^2H/dx^2 = 100\ \mathrm{N\ m^{-1}}$), the chain length ($l = 7.49$ Å), and the cross-sectional area ($\sigma = 18.4$ Å) is 407 ± 20 GPa. Estimates of the tensile moduli using clusters of 4, 8 and 10 CH_2 units yielded similar values (*Table 1*). The confidence interval of 20 GPa is based on the accuracy of the numerical derivative, the cross-sectional area and length.

Electron correlation is known to be important in the calculation of vibrational spectra since the Hessian of a single-determinant SCF wavefunction always overpredicts experimental frequencies[16]. This overprediction is intimately related to the calculated bond stiffness and thus the Young's modulus. One might argue that the AM1 parameterization, which uses experimental data, accounts for the correlation energy and thus should accurately predict vibrational frequencies. A comparison of the calculated and observed frequencies for hexane shows that this is not the case. *Figure 2* compares the AM1 and MP2/6-31g frequencies with the spectrum inferred from vibrational spectroscopy of hexane and its deuterated analogues[17]. A least-squares fit of the computed frequencies yields comparable slopes for the AM1 (1.054) and MP2 (1.064) approaches. However, the error in the correlated *ab initio* calculations is systematic: they always overpredict the frequency. By

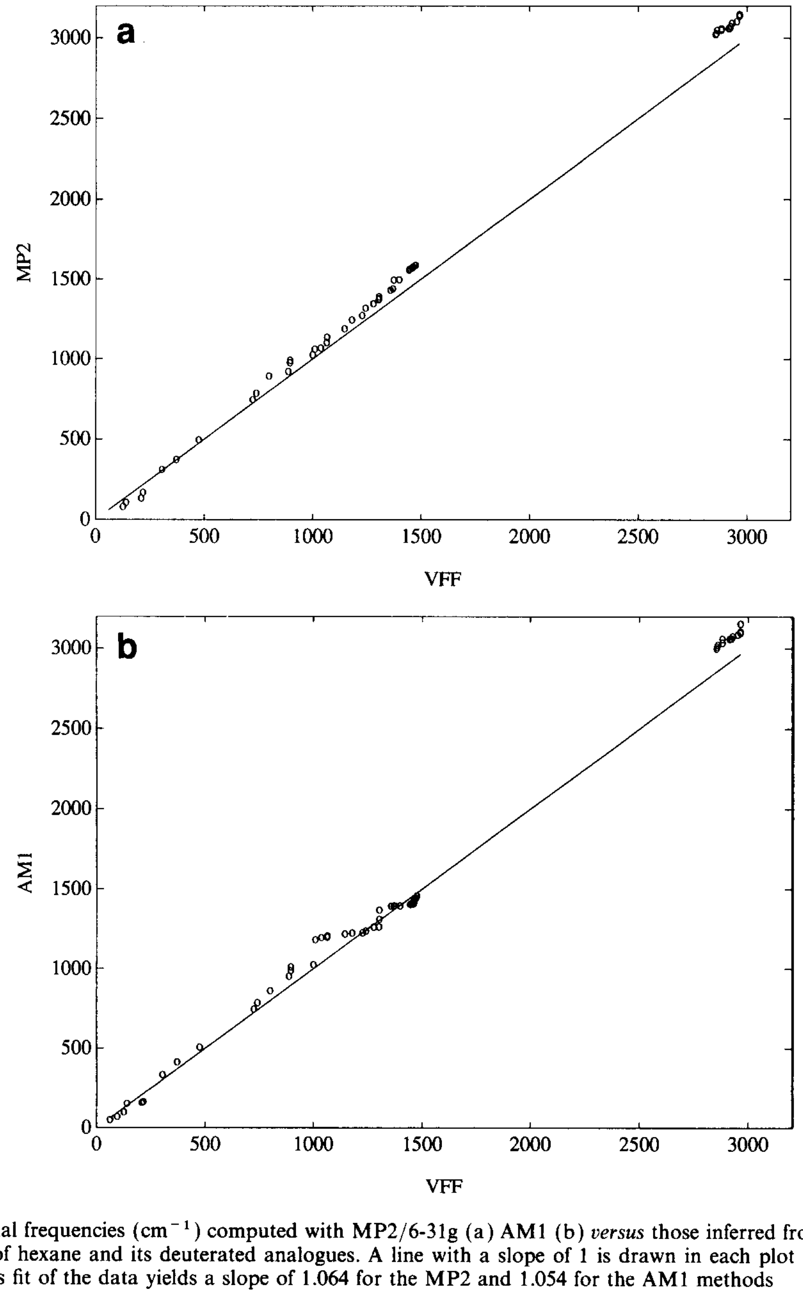

Figure 2 Plots of vibrational frequencies (cm^{-1}) computed with MP2/6-31g (a) AM1 (b) *versus* those inferred from a valence force field (VFF) derived from spectroscopy of hexane and its deuterated analogues. A line with a slope of 1 is drawn in each plot to facilitate comparison of the errors. A linear least-squares fit of the data yields a slope of 1.064 for the MP2 and 1.054 for the AM1 methods

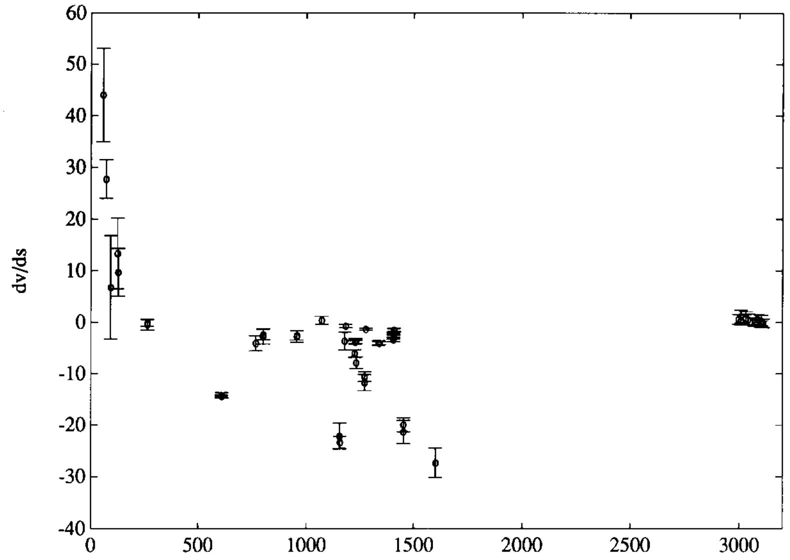

Figure 3 Variation of computed vibrational frequencies with strain. A linear least-squares fit yields $d\nu/d\Delta$. The error bars represent the square root of the sum of the squared error of the linear fit over seven strain values

contrast, the AM1-computed frequencies have random error: they both under- and overpredict the correct frequency. In particular the AM1 C–C bending modes (1000–1500 cm^{-1}) are as much as 5% softer than observed experimentally.

Some of the vibrational frequencies shift when the system is strained. *Figure 3* displays the results of a linear least-squares fit of the computed strain dependence, $d\nu/d\Delta$, to 0.5% strain; error bars indicate the root mean square error of the linear fit. The transverse modes below 500 cm^{-1} have frequencies which increase with strain, much as the pitch of a violin string increases when tensed. All of the remaining modes are predicted to either decrease or remain constant with tension. There is no correlation of $d\nu/d\Delta$ with the harmonic frequency of the unperturbed mode.

The stress dependence of Raman-active stretches at $\nu_{as} = 1063$ cm^{-1} and $\nu_s = 1127$ cm^{-1} have been reported[18–20]. These modes have equilibrium frequencies of $\nu_{as} = 1155$ cm^{-1} and $\nu_s = 1270$ cm^{-1} in the AM1 calculations. They both decrease linearly with strain to 4% strain in the calculations. Conversion of the computed strain-dependent frequencies to the observed stress-dependent values requires division by the appropriate modulus. The values summarized in *Table 3* suggest that the calculation has captured the essential physics of the frequencies' strain dependence. The computed values of $d\nu/ds$ are within the bounds of those observed experimentally for ν_{as} and ν_s. Further, the ratio of the strain dependence for the symmetric and asymmetric modes is comparable in all the experiments and the calculation. A closer examination of the experimental results finds no perceptible shift in the C–H stretching region above 2800 cm^{-1}, the methylene rock at 1168 cm^{-1}, or the twist at 1295 cm^{-1}, in agreement with the AM1 calculations. The poorest agreement between experiment and theory is among the infra-red-active stretching modes near 1470 cm^{-1}, where one report[19] of $d\nu/d\Delta \approx -2.6$ (cm%)$^{-1}$ is substantially less than the computed value of 20 (cm%)$^{-1}$.

The variation of frequency with strain does not correlate with the projection of the strain vector on the normal modes. *Figure 4a* illustrates the projection of the

Table 3 Strain dependence ($d\nu/d\Delta$) of the Raman-active modes at 1064 and 1127 cm^{-1} inferred from the reported stress-dependent frequency shifts ($d\nu/ds$). Using the calculated modulus the AM1 stress dependencies are in reasonable agreement with experimental values

ν_{as}, ν_s (cm^{-1})	$d\nu/ds$ (cm GPa)$^{-1}$	Modolus (GPa)	$d\nu/d\Delta$ (cm%)$^{-1}$	Ref.
1064	−6.0	240	−14.5	20
1064	−11.2	267	−29.9	19
1064	−4	200	−8	18
AM1	−5.8	400	−23	
1127	−4.5	240	−11	20
1127	−5.9	267	−17	19
1127	−2.5	200	−5	18
AM1	−2.8	400	−11	

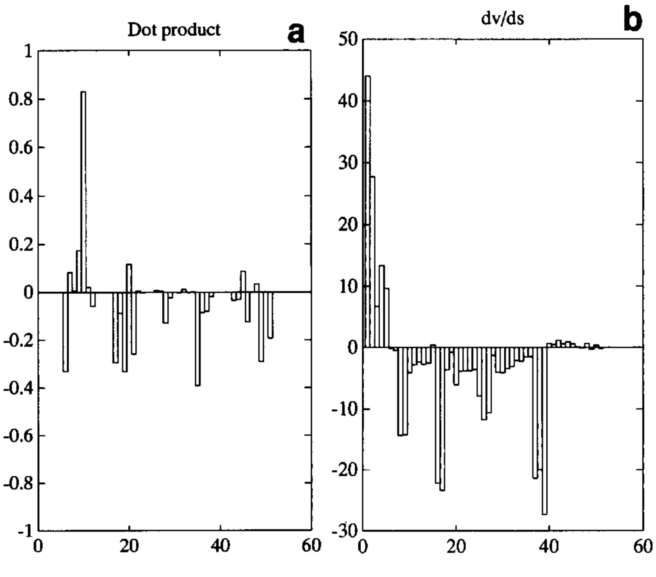

Figure 4 (a) Dot product of each of the 51 eigen-vectors (in order of increasing frequency) for the equilibrium system with the strain vector. (b) Bar graph with the same abscissa as (a) showing the calculated values of $d\nu/d\Delta$. The dot product and strain dependence are uncorrelated

equilibrium normal modes onto the strain vector, while the strain dependence is displayed in *Figure 4b*. Some modes which are affected by strain have a large projection onto the strain vector while others do not.

Based on the observed stress dependence of polyethylene vibrational frequencies, Wood and Bretzlaff[19] constructed a Morse-oscillator model for polyethylene. The C–C potential in this model has a second derivative at equilibrium of 440 N m^{-1}. Varying only one C–C bond length in the cluster while optimizing all other distances and angles yields an AM1 second derivative for the C–C bond of 580 ± 20 N m^{-1}, which is 30% higher than that inferred from spectroscopy.

DISCUSSION

Among the ways of examining the quantum mechanical basis for polymer properties are *ab initio* calculations on gaseous oligomers, extended Huckel band structure calculations, and molecular mechanics approaches based on empirical potentials. Each of these methods has advantages and disadvantages. Our purpose here is to explore some of the strengths and weaknesses of the semi-empirical quantum approach to the microscopic basis for polymeric properties. Specifically, we have examined the geometries, tensile moduli, equilibrium vibrational frequencies and their variation with strain for polyethylene.

The agreement between calculated and experimental equilibrium geometries is quite remarkable. Although a full map of the potential energy surfaces on distortion has not been performed, the distances and angles found using AM1 compare favourably both with experiment and with more elaborate electronic structure calculations.

Moving away from equilibrium, careful experimental measurements of the Young's modulus vary from 221 to 358 GPa (*Table 4*). The measurement techniques include X-ray diffraction[21,22], mechanical testing[23], neutron scattering[24] and Raman spectroscopy of oligomers[25,26]. In each of these experiments, care was taken to account for the influence of amorphous contributions in estimating the modulus of crystalline polyethylene. The modulus of polyethylene has also been calculated using the MNDO semi-empirical method[27] and a small-basis *ab intio* approach[28]. The MNDO method led to a modulus of 360 GPa, while the *ab initio* report found a modulus of 400 GPa, in surprising agreement with the present result. More recently a biased Hessian force field for polyethylene has been described[29] which yields a modulus of 337 GPa.

Table 4 Experimental and calculated c-axis moduli for polyethylene. The AM1 modulus is 407 ± 20 GPa

Modulus (GPa)	Method	Ref.
235	X-ray	21
221	X-ray	22
240	Fibre pull	20
288	Fibre pull	23
267	I.r./Raman	19
329	Neutron	24
358	Raman	25
290	Raman	26
278	Average	
337	Biased SCF	29
360	MNDO	27
400	*ab initio*	28

The AM1 modulus is larger than the largest measured value and 40% larger than the average experimental result. It might be argued that the electronic structure calculations yield an ultimate modulus for a material without morphological or stoichiometric defects, so that overprediction of the measured modulus is to be expected[8]. An alternative is that systematic errors in the AM1 UHF calculations lead to overestimates of the bond stiffness and thus the tensile modulus.

The systematic error associated with single determinant *ab initio* description of molecular force fields is thoroughly documented[16] but often overlooked when semi-empirical methods are employed. One common approach[30] is to scale all of the Hartree–Fock frequencies by a constant factor of about 0.9. This approach is quite successful when computing zero-point contributions to the enthalpy. More sophisticated methods of scaling the Hartree–Fock Hessian using observed frequencies have also been developed[31,32]. For systems with large exact excitation energies, singlet-stable solutions for the Hartree–Fock ground state, and localized molecular orbitals, there is good theoretical justification for scaling the Hessian[33]. A biased Hessian approach has recently been applied to generate a force field for polyethylene using a butane oligomer[29]. Application of a biased MOPAC Hessian to strained polyethylene will be taken up in a separate publication[34].

The AM1 UHF Hamiltonian should not be expected to give a quantitatively accurate Hessian matrix:

$$\mathscr{H}_{ij} = \frac{\mathrm{d}^2 H}{\mathrm{d}x_i \mathrm{d}x_j}$$

since it is a single-determinant calculation. Overestimation of the equilibrium vibrational frequencies by about 5% indicates that the AM1 Hessian is too stiff. Comparison of the AM1 and MP2 frequencies for hexane show that the correlation effects required to accurately describe the Hessian are not implicit in the semi-empirical parameterization. This systematic overestimate of the intramolecular stiffness translates into overestimates of the tensile modulus and the frequencies at zero strain.

Another argument for the exaggerated stiffness of the AM1 UHF Hessian arises from comparison with molecular mechanics potentials which reproduce the vibrational spectrum of polyethylene to high precision. The biased Hessian force field[29] yields a modulus at room temperature of 322 GPa, 20% less than found using AM1. Further, when simulating a single C–C bond with AM1 we find that $\mathrm{d}^2H/\mathrm{d}x^2$ is about 30% larger than that inferred from a Morse-oscillator force field[19].

The present results suggest that care should be taken when using potentials derived from the UHF semi-empirical electronic structure codes for molecular dynamics simulations. Systematic overestimates of bond stiffness due to neglect of electron correlation should cause concommitant changes in the dynamics. It is preferable to either include correlation in an appropriate way or scale the Hessian to get numerical energy derivatives in accord with nature.

The semi-quantitative prediction of the strain dependence of harmonic frequencies indicates that the AM1 Hamiltonian does a reasonable job of describing the anharmonicity of the bonds. The strain dependence is proportional to the component of the anharmonicity which projects onto the strain coordinate x_s:

$$\frac{d\nu}{d\Delta} \propto \frac{d}{dx_s}\sqrt{\frac{d^2E}{dx_i\,dx_j}}$$

It is not inconsistent that the calculations overestimate the second derivatives while providing reasonable third derivatives. The numerical influence of the overestimated Hessian elements is cancelled when dividing by the computed modulus to compare with experimental stress dependencies. Thus the AM1 approach may be very useful in identifying which modes in a polymer are likely to produce experimentally observable frequency shifts with strain.

An exciting aspect of the computational approach is that all modes can be examined in a balanced way, independent of oscillator strengths, band overlap, impurities and defects which cause spectral features away from the zone centre. It may also be possible to deconvolute the role played by individual bonds in strained polymers.

CONCLUSION

The tensile modulus and strain dependence of vibrational frequencies in polyethylene have been computed using a semi-empirical cluster model with an AM1 Hamiltonian. On comparison with experimental data and correlated *ab initio* calculations the intramolecular forces are found to be systematically overestimated, leading to overpredictions of the tensile modulus. The anharmonicity of the bonds is well characterized by the AM1 potentials based on the agreement of calculated and observed variations of vibrational frequencies with strain.

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