

The stiffness of a fully stretched polyethylene chain: A Raman jet spectroscopy extrapolation

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Linear alkanes with $n=5-16$ C-atoms are partially relaxed into their stretched *all-trans* conformation by supersonic jet expansion. Their longitudinal acoustic modes are identified by spontaneous Raman scattering and deperturbed from transverse bending mode components and Fermi resonance with combination states of the same symmetry. Comparison with quantum chemical predictions of the longitudinal modes in hydrocarbon chains with up to 54 C-atoms allows for a reliable extrapolation to the limiting product $n \cdot \tilde{\nu}_n = 2310 \pm 30 \text{ cm}^{-1}$ for large n , from which the elastic modulus of an ideal polyethylene chain in vacuum may be estimated at $309 \pm 8 \text{ GPa}$. Differences to solid state determinations of this quantity are discussed. © 2009 American Institute of Physics. [doi:10.1063/1.3256221]

Polyethylene is among the most abundant and structurally simplest polymer materials. It is desirable to have an accurate experimental value for its elastic (or Young's) modulus E along the infinite chain, free of any influence from neighboring chains. Such a number can best be compared with quantum theory¹ and it provides a benchmark for high-modulus polymer materials. Previously, the elastic modulus has been estimated by Raman spectroscopy of the longitudinal acoustic modes (LAMs) in finite length alkanes in the solid state and was found to be close to $358 \pm 25 \text{ GPa}$.² Such a crystalline solid state approach has the advantage of forcing the alkanes into lamella of stretched *all-trans* conformation by crystal forces. The LAMs are known to be sensitive spectroscopic probes for this *all-trans* motif, also in bulk polyethylene.³ However, the solid state method suffers from the influence of neighboring lamellae and of neighboring molecules within the lamellae. Corrections for the former effect have been attempted⁴ and yield $E \approx 290 \text{ GPa}$. Later, these corrections have been amended to yield $E = 305 \pm 3 \text{ GPa}$.⁵ Still, a comparison with alternative determinations of the elastic modulus of polyethylene (e.g., 240 GPa from x-ray analysis of crystalline polymer segments under stress⁶) is somewhat unsatisfactory⁷ and the influence of neighboring chains as well as imperfections of the polymers are likely reasons for this indeterminacy. We note that the actual specimen modulus of polyethylene material can vary over more than an order of magnitude depending on the preparation and it typically falls short of the ideal elastic modulus by more than two orders of magnitude.¹ Nevertheless, polyethylene fibers with a modulus of 262 GPa at 77 K have been produced by special procedures.⁸ After correction for instrumental effects, an improved E value of $288 \pm 10 \text{ GPa}$ was deduced.⁸ In order to assess how far

away such a macroscopic value is from its fundamental limit, a reliable indirect experiment is required.

In this work, we take a gas phase approach to the problem. Expansion of linear alkanes C_nH_{2n+2} with sufficient vapor pressure in a He or Ne carrier gas through a slit nozzle relaxes the multitude of chain conformations into the stretched *all-trans* form, which represents the global minimum for not too long alkanes, such as in the elementary butane case.⁹ There will actually be a point where non-stretched, chiral conformations take over the global minimum property,¹⁰ even in the absence of solvent or encapsulation effects.¹¹ Here, we make use of our experimental observation that *all-trans* conformations appear to dominate the low-temperature gas phase at least up to $C_{16}H_{34}$, which is within recent theoretical estimates.^{12,13} We note that chain-folding in the solid is shifted in n by at least an order of magnitude,¹⁴ because the energetic driving force is lost.

Low temperatures are essential for a gas phase approach to the elastic modulus, because in chains as short as pentane at room temperature the *all-trans* conformation is no more the dominant one for entropic reasons.^{15,16} The efficient conformational relaxation to the *all-trans* state in the supersonic jet allows for the spectral identification of the corresponding LAMs.² Although we observe weak transitions from higher-order modes as well, the present analysis concentrates on the lowest energy, single node vibration, where the two chain halves stretch and compress in phase relative to the center of the molecule. These modes, also called accordion modes, are easily identified due to their high Raman activity. Their wavenumber is roughly proportional to $1/n$. Raman spectroscopy in gases, including supersonic jet expansions, is now a mature field.¹⁷ However, it has rarely been applied to larger molecules. A recent gas phase study of pentane¹⁸ has actually been triggered by the present investigation. Previous low frequency Raman spectroscopy of alkanes in jets was restricted to ethane¹⁹ and its torsional levels.²⁰

In our experiments, a slit jet expansion is probed by a 532 nm laser (18W Verdi, Coherent) and the scattered radia-

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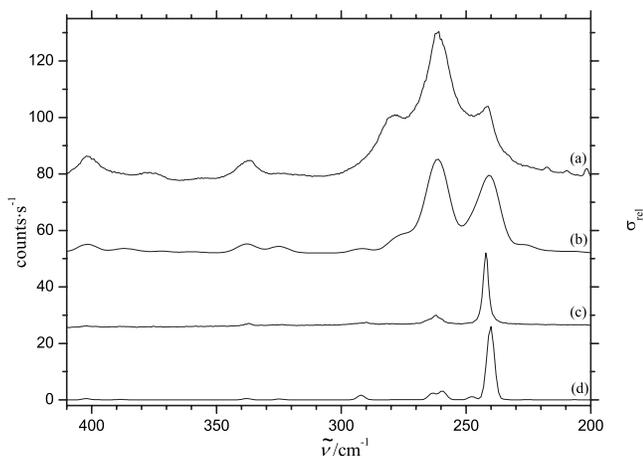


FIG. 1. Experimental Raman spectra of n -nonane in (a) the gas phase and (c) in a supersonic jet expansion (0.2% in He, 0.7 bar, and 2 mm away from the nozzle). Statistical simulations based on B3LYP conformational energies and harmonic predictions, corresponding to effective conformational temperatures (line widths) of (b) 300 K (9 cm^{-1}) and (d) 140 K (3.5 cm^{-1}) are shown below the experimental spectra. The spectra are scaled to similar LAM peak height.

tion is collected and dispersed after suppression of the Rayleigh scattering by a suitable edge filter. For experimental details, see Refs. 21 and 22. The spectra are complemented by quantum chemical calculations at HF/3-21G and B3LYP/6-311+G(d) levels.²³

Typical spectra for nonane ($n=9$) are displayed in Fig. 1. Trace (a) shows the room temperature gas phase spectrum, whereas trace (c) exemplifies the simplification by supersonic jet expansion. Much of the population is shifted toward the *all-trans* conformation with its characteristic LAM near 240 cm^{-1} . A statistical rotational isomeric state simulation [trace (d)] based on ten conformations, but neglecting small differences in rotational and vibrational partition function except for the symmetry number, indicates that the conformational temperature is close to 140 K in this case. The room temperature gas phase simulation (b) includes in addition free enthalpy corrections for the individual conformations within the rigid-rotor harmonic oscillator model implemented in GAUSSIAN. The difference to a simulation neglecting this correction [such as in trace (d)] is less than 20% at 300 K but becomes more significant at higher temperatures. Comparison with trace (a) shows that there are still intensity, model, or relative energy deficiencies²⁴ in this approach. In particular, the *all-trans* population is somewhat overestimated.

The resulting experimental LAM wavenumbers are listed in Table I as a function of n . In some cases, the scattering intensity is shared by a nearby transverse acoustic mode (TAM) of the same symmetry involving several nodes. This mode is listed in parentheses, where it could be identified. Such mode mixing is reproduced quite well within the harmonic approximation for several electronic structure levels. In the case of $n=14$, anharmonic Fermi resonance with a combination band (two B_u backbone vibrations near 26 and 135 cm^{-1}) was also observed. Both kinds of mode mixing have been approximately removed by a standard first order deperturbation technique,²⁵ assuming that the scattering in-

TABLE I. Experimental and B3LYP/6-311+G(d), as well as HF/3-21G values for longitudinal acoustic modes (in cm^{-1} , harmonic perturbors in parentheses, Fermi resonance pair in brackets) of linear alkanes from 5 to 16 C-atoms.

n	Expt.	B3LYP	HF
5	399	398	421
6	367 (292–302)	366 (297)	390 (321)
7	303 (418)	301 (419)	317 (454)
8	276 (196)	274 (195)	287 (212)
9	242 (290)	240 (292)	252 (316)
10	223 (133)	222 (133)	232
11	194 (212)	196 (214)	207 (229)
12	185	186	195
13	175 (149)	174 (153)	183 (165)
14	[164] [157]	161	168
15	151	151 (119)	158 (129)
16	144	141 (169)	148 (183)

tensity is solely due to the LAM. If the closest perturber could be identified in the experimental spectrum, it was taken into account. In the calculations, this was done if the acquired Raman activity of the perturber exceeded 0.1 $\text{\AA}^4/\text{u}$. In this way, the unperturbed LAM wavenumber could be estimated. The success of the deperturbation procedure is illustrated in Fig. 2 for model calculations of odd-membered alkanes extending to 53 C-atoms, using the simple HF/3-21G approach and plotting the product of the wavenumber $\tilde{\nu}_n$ and the chain length n . One can see how the original harmonic predictions (filled circles for the LAM, filled triangles for the perturber modes shown schematically with their node structure) behave irregularly in some places, whereas the deperturbed LAM values (open circles) interpolate smoothly to a limiting value for large n . Very similar results were obtained for the even-membered chains, which couple to different TAMs.

In Table I, the original (perturbed) HF/3-21G harmonic predictions as well as corresponding B3LYP/6-311+G(d) values are compared with experiment. Clearly, the B3LYP

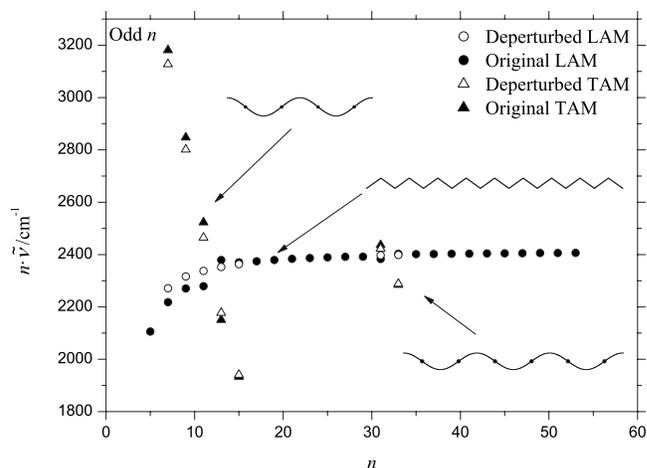


FIG. 2. Illustration of the deperturbation approach for odd $n < 55$ at the HF/3-21G level. The LAM mode wavenumbers (zigzag symbol for the stretched alkane) converge to about 2400 cm^{-1}/n , but there are mode mixings with TAM modes containing four and six nodes (symbolized by sinusoidal lines), which are removed by deperturbation (open symbols).

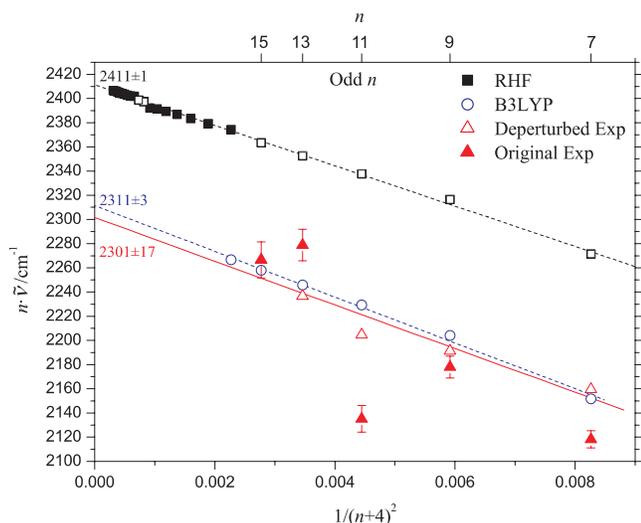


FIG. 3. Asymptotic extrapolation of computed and experimental LAM modes to infinite n for odd members of the alkane series, see text for explanations. Open symbols represent values resulting from a deperturbation procedure, which was not necessary for $n=15$.

approach offers an excellent agreement, almost within the accuracy of the experimental wavenumbers. This also allows for a testing of the deperturbation procedure under realistic conditions, except for the Fermi resonance for $n=14$, which is of course absent in the harmonic treatment. Thus, the experimental data can be checked and extended using this level of approximation.

To obtain a reliable extrapolation to $n=\infty$ with little model bias and few variable parameters,² we have modified the model expression employed before²

$$n \cdot \tilde{\nu}_n = A + B/n^2 + \dots,$$

by plotting the product of chain length and LAM wavenumber against $1/(n+4)^2$. This turns a curved plot of the HF results into a nearly straight line for $n < 54$, which is shown in Fig. 3 for odd n . The shift in n by four units takes into account the higher order deviations from the asymptote, whereas B reflects the first order deviations, all caused by the existence of end groups in the chains. The validity of this approach is confirmed by the fact that the smaller B3LYP data set also falls on a linear extrapolation, which is almost parallel to the HF one. We refrain from attaching a physical meaning to the slope, whereas the intercept parameter A is directly related to the elastic modulus E (*vide infra*). The linear fits only include alkanes with $n > 6$ where the accordion mode character starts to become dominant. A corresponding fit can be carried out for the even-membered chains (not shown). We tried several other polynomial and linear fits with similar results, but the proposed model yielded by far the smallest changes in the A intercept, when the database was reduced from $n=54$ to $n < 17$, the experimental limit currently dictated by the vapor pressure of the alkanes. Note that the deperturbation of the experimental LAM wavenumbers is essential, as the difference between filled and open symbols shows. For the quantum chemical data, perturbed points are not shown where a deperturbation was carried out (open symbols).

TABLE II. Fitted asymptotes A (in cm^{-1}) and their statistical error bars ΔA for different databases and n -ranges of odd (o) and even-numbered (e) alkanes $\text{C}_n\text{H}_{2n+2}$.

Database	n_l-n_u	o/e	A/cm^{-1}	$\Delta A/\text{cm}^{-1}$
HF	7–53	o	2411	1
HF	8–54	e	2413	1
HF	7–15	o	2411	1
HF	8–16	e	2417	4
B3LYP	7–17	o	2311	3
B3LYP	8–18	e	2320	3
Expt.	7–15	o	2301	17
Expt.	8–16	e	2326	27

Table II summarizes the A parameters obtained from fits to experimental and theoretical data sets for ranges of chain length n_l-n_u . Several observations can be made. Even-membered alkanes have a slight bias toward higher A values, if the fit is truncated at short chains. After deperturbation, the experimental extrapolation error is on the order of the calibration and peak uncertainties of the long chain spectra. The B3LYP prediction is consistently lower than the HF finding.

Based on this, one may estimate an experimental value of $A=2310 \pm 30 \text{ cm}^{-1}$. Most of the remaining error stems from the limited convergence of the even and odd values when the data set is truncated at $n=16$. However, larger n values face several limitations: The vapor pressure requires the use of a heated nozzle, the *all-trans* conformation ceases to be the global minimum structure and the calibration error is further amplified by a factor of n . Therefore, we consider the present data set as a good compromise. Inclusion of LAMs with more nodes^{2,4} may lead to further improvements.

A can now be related to the elastic modulus E (at low temperature²⁶) of a “one-dimensional” macroscopic bar by

$$A = \frac{1}{2cd} \sqrt{\frac{E}{\rho}}.$$

Here, c is the speed of light, ρ is the density of the mechanical bar, and d is the segment length along the chain dimension. The latter two quantities stem from the translation to continuum mechanics and carry substantial arbitrariness, but reasonable estimates can be made. A value of 1.00 kg dm^{-3} for the density of polyethylene has often been used.^{4,5} For the segment length, 127 pm is a frequently used value,^{4,5} which we shall adopt here for consistency. We note however, that there is a variance and uncertainty on the order of 1% in the appropriate d^2 and ρ values to be employed.² Therefore, it may not be meaningful to quote the derived E values to better than 1%–2%.

From this, one obtains a prediction for the elastic modulus of $E=309 \pm 8 \text{ GPa}$. This is significantly lower than the value derived originally from alkane crystals² (358 GPa) but it is rather close to an improved evaluation, which attempts to include packing effects of the chains⁴ ($\approx 290 \text{ GPa}$) and it is in agreement with a further improved value ($305 \pm 3 \text{ GPa}$) involving extensive solid state corrections and very long alkane chains.⁵ Our value is significantly higher than inelastic neutron scattering and x-ray diffraction results⁶ (see also a

compilation in Ref. 1), which both involve lateral interactions with neighboring chains. A recent claim²⁷ that the highest experimental value is 324 GPa cannot be confirmed by us. In view of the temperature dependence of the elastic modulus, our spectroscopic value may be considered as a 0 K result, although the jet-cooled alkanes have some residual thermal excitation. The LAM peak positions are not expected to change much with further cooling and the rotational temperature is certainly below 50 K. The LAM excitation itself vanishes in the limit of an infinite chain.

One can also extract the theoretical elastic modulus from an investigation of stretched alkanes²⁸ or infinite polyethylene,²⁹ thus circumventing the normal mode analysis. If electron correlation is included, a very close prediction of 303 GPa can be obtained already at a small basis set MP2 level.²⁹ This is confirmed by the present hybrid density functional B3LYP predictions, whereas our own exploratory MP2/6-311+G(d) harmonic predictions tend to be a few percent higher than the experimental accordion vibrations. On the other hand, a more recent DFT Car-Parrinello study³⁰ predicts 334–337 GPa, clearly too high in line with known deficiencies of the local density approximation (LDA). A very recent LDA determination of the chain modulus of 360 GPa (Ref. 27) is also inconsistent with our results. It is noteworthy that crystal simulations with “better,” gradient-corrected density functionals fail to capture the interchain interactions,²⁷ but we predict that they should provide more reasonable results for isolated chains.

In summary, the elastic modulus of an isolated polyethylene chain in vacuum has been determined by extrapolation of the LAMs of *n*-alkanes with 7–16 C-atoms to infinity. It has a value of 309 ± 8 GPa, orders of magnitude larger than measured for most real stretched polymer samples and still significantly larger than estimated by x-ray crystallography. This represents a rigorous benchmark for high-modulus polyethylene materials which is amenable to very high-level quantum chemistry modeling due to its stepwise chain extension approach.

Although the simple harmonic B3LYP approach has some fundamental deficiencies for alkanes²⁴ and will fail for the folding problem,¹² it turns out to match experimental accordion vibrations remarkably well and may thus be used to interpolate, extrapolate and analyze the Raman spectroscopic data. Our future efforts in this field will be directed toward identifying the critical chain length which starts to fold in vacuum in order to minimize its energy.¹²

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