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Coupled Cluster Study of the Linear Carbon Chains C_{2n+1} ($n = 5-9$)[†]

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Making use of the coupled cluster variant CCSD(T) in conjunction with Dunning's cc-pVTZ basis set, equilibrium structures and complete harmonic force fields have been calculated for the linear carbon chains of type C_{2n+1} with $n = 5-9$. With the exception of C_3, which is a well-known "floppy" molecule with an extremely shallow bending potential, all members of the C_{2n+1} series up to C_{19} appear to behave like fairly normal semirigid molecules. The IR active bending vibrations of lowest wavenumber for C_{17} and C_{19}, which may be of interest to forthcoming far-infrared astronomy, are predicted to occur at 13.1 and 11.1 cm^{-1}, respectively, with corresponding absolute IR intensities of 6.6 and 5.9 km mol^{-1}. Huge IR intensities are calculated for one antisymmetric stretching vibration per chain (19 948, 29 632, and 30 040 km mol^{-1} for C_{15}, C_{17}, and C_{19}, respectively). A quantitative description of these vibrations may require the explicit consideration of anharmonicity effects and electronic structure calculations going beyond CCSD(T).

1. Introduction

Owing to their importance to combustion processes and astrochemistry, pure carbon chains have been the subject of various experimental and theoretical studies (see, e.g., ref 1 for a review). At present, linear C_{13} is the only chain with more than 10 atoms for which a high-resolution spectrum could be obtained. Two research groups were able to study rovibrational transitions within the strong ν_9 band in the range between 1808 and 1810 cm^{-1},[2,3] both making use of diode laser infrared (IR) spectroscopy. For still larger carbon chains, published spectroscopic information is scarce. It involves electronic spectra of odd-number carbon chains, observed in a neon matrix at 6 K,[4−6] and UV−vis and IR absorption data from selective oxidation experiments in oxygen matrixes,[7] with linear C_{21} being the longest chain for which assignments were made. Such cumulenic chains with the general formula C_{2n+1} are closed-shell molecules with electronic ground states of $^1\Sigma_g^+$ symmetry. As is well-known (see, e.g., ref 8), the smallest member of this class of carbon chains, C_3, is a rather floppy molecule with an extremely shallow bending potential and may be termed a quasi-linear molecule. A spectroscopic indicator of such a situation is provided by the percentage change of the rotational constant occurring upon excitation of one quantum of the lowest bending vibration. For C_3, it is as high as 3.4%. A still much larger increase of 9.3% was reported for linear C_7 by Heath and Saykally on the basis of an analysis of their diode laser IR absorption spectra.[9] However, coupled cluster calculations carried out by the author yielded a much smaller value of 0.2% and showed no evidence of particular floppiness for this carbon chain.[10,11] Quite recently, the author's theoretical predictions were nicely confirmed by more extensive spectroscopic work at Cologne.[12] During the past two years, the author has theoretically investigated the bending potentials of linear C_{2n+1} chains up to C_{15}[13,14] and arrived at the conclusion that all of those species with $n > 1$ are fairly normal semirigid molecules. Likewise, no indication of floppiness was found in a theoretical investigation of linear carbon chains of type C_{2n} up to C_{10},[15] which have electronic ground states of $^3\Sigma_g^-$ symmetry and may also be classified as cumulenic systems with short CC double bonds.

TABLE 1: Comparison of CCSD(T)/vtz and CCSD(T)/vqz Harmonic Vibrational Wavenumbers for Linear C_{11}

vibration	vtz	vqz[a]	vibration	vtz	vqz[a]
ω_1 (σ_g)	2220.1	2220.5	ω_6 (σ_u)	2180.8	2184.6
ω_2 (σ_g)	2054.8	2061.2	ω_7 (σ_u)	2043.4	2040.8
ω_3 (σ_g)	1654.8	1664.8	ω_8 (σ_u)	1882.9	1891.5
ω_4 (σ_g)	1049.4	1056.8	ω_9 (σ_u)	1359.1	1368.0
ω_5 (σ_g)	370.3	372.9	ω_{10} (σ_u)	721.6	726.6
ω_{11} (π_g)	519.2	510.1	ω_{15} (π_u)	518.3	509.7
ω_{12} (π_g)	445.8	439.7	ω_{16} (π_u)	487.2	482.2
ω_{13} (π_g)	215.3	208.3	ω_{17} (π_u)	273.1	263.8
ω_{14} (π_g)	83.0	81.5	ω_{18} (π_u)	148.2	144.3
			ω_{19} (π_u)	31.9	31.5

[a] Reference 14.

The present paper extends the author's previous work to linear C_{2n+1} chains up to C_{19}, making use of coupled cluster calculations at a uniform level such that proper comparison among the results for different chains is possible. Throughout, complete harmonic force fields have been calculated from which the whole set of harmonic vibrational wavenumbers has been obtained. Particular emphasis will be given to the absolute intensities of the IR active vibrations and to the bending potentials of linear C_{17} and C_{19}, which have been studied by coupled cluster calculations for the first time.

2. Details of Calculations

The coupled cluster variant CCSD(T)[17] in conjunction with Dunning's cc-pVTZ (or vtz, for brevity) basis,[18] comprising 30 contracted Gaussian-type orbitals (cGTOs) per carbon atom, was employed to calculate equilibrium structures and harmonic force fields for linear C_{2n+1} chains with $n = 5-9$. Throughout, valence electrons were correlated in the calculations which were carried out with the MOLPRO suite of programmes.[19−21]

The harmonic force fields were calculated numerically from CCSD(T) energy points, using distortions out of equilibrium of ±0.002 Å for bond lengths and ±1° for bond angles. They

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TABLE 2: CCSD(T)/cc-pVTZ Equilibrium Structures for Linear Carbon Chains C_{2n+1} ($n = 6-9$)[a]

	C_{13}		C_{15}		C_{17}	C_{19}
	recomm. [13]	CCSD(T)/vtz [22]	recomm. [13]	CCSD(T)/vtz	CCSD(T)/vtz	CCSD(T)/vtz
R_{1e}	1.2886	1.2960(0.0074)	1.2883	1.2957(0.0074)	1.2954	1.2952
R_{2e}	1.2919	1.2978(0.0059)	1.2928	1.2986(0.0058)	1.2993	1.2998
R_{3e}	1.2694	1.2760(0.0066)	1.2690	1.2756(0.0066)	1.2752	1.2748
R_{4e}	1.2800	1.2862(0.0062)	1.2811	1.2873(0.0062)	1.2882	1.2888
R_{5e}	1.2736	1.2800(0.0064)	1.2729	1.2793(0.0064)	1.2788	1.2783
R_{6e}	1.2767	1.2831(0.0064)	1.2782	1.2846(0.0064)	1.2856	1.2864
R_{7e}			1.2757	1.2821(0.0064)	1.2814	1.2808
R_{8e}					1.2835	1.2845
R_{9e}						1.2827
R_{10e}						

[a] Differences with respect to recommended values are given in parentheses.

are represented in conventional normalized symmetry coordinates S_i, where S_1-S_n refer to symmetric stretching coordinates of σ_g symmetry, $S_{n+1}-S_{2n}$ refer to antisymmetric stretching coordinates of σ_u symmetry, $S_{2n+1}-S_{3n-1}$ refer to trans-bending coordinates of π_g symmetry, and $S_{3n}-S_{4n-1}$ refer to cis-bending coordinates of π_u symmetry. In the definition of coordinates S_i, carbon−carbon bonds and CCC angles are counted from outermost to innermost.

The performance of CCSD(T)/cc-pVTZ for the harmonic vibrational wavenumbers was checked for linear C_{11} against the results of calculations with the almost twice as large cc-pVQZ (or vqz) basis set (55 cGTOs per carbon atom). Comparison of the CCSD(T) results as obtained with the two basis sets is made in Table 1. For the stretching vibrations of both σ_g and σ_u symmetry, the CCSD(T) calculations with the smaller basis set yield smaller values by up to 10 cm^{-1}, with the mere exception that the CCSD(T)/cc-pVTZ value for ω_7 (σ_u) is calculated to be larger by 2.6 cm^{-1}. For all of the bending harmonic vibrational wavenumbers, the results obtained with the cc-pVTZ basis are overestimates with the respect to those obtained by CCSD(T)/cc-pVQZ, but the difference is again never larger than 10 cm^{-1}.

Absolute IR intensities of the IR active vibrations of σ_u and π_u symmetry were calculated within the familiar double-harmonic (DH) approximation, which requires the knowledge of the first dipole moment derivatives with respect to the symmetry coordinates, evaluated at the equilibrium structures. Throughout, these calculations were carried out at the recommended equilibrium geometries from the present and previous work.[13,22] At the CCSD(T) level, the correlation contributions to the electric dipole moments were calculated as numerical derivatives of the correlation energies with respect to the strength of a uniform electric field of ±0.0001 atomic units (au), applied either along the molecular axis or perpendicular to it. These were then added to the corresponding Hartree−Fock values, obtained as expectation values, to yield the total dipole moments. Displacements of ±0.005 Å for antisymmetric stretching coordinates and 2° for cis-bending angular coordinates were employed in the numerical calculation of the dipole moment derivatives.

In the calculation of first dipole moment derivatives, a uniform basis was employed. It consists of the spd part of Dunning's cc-pVTZ basis set,[18] augmented by the corresponding diffuse functions at the terminal carbon atoms from the aug-cc-pVTZ basis set.[23] Thereby, a better description of the lone pairs at the carbene-like end atoms is achieved. In the following, this basis will be termed spd(cc-pVTZ/spd(aug-cc-pVTZ) or just "small". For the smaller carbon chains up to C_{13}, the performance of this basis was checked against results obtained with the much larger basis spdf (cc-pVQZ)/spdf (aug-cc-pVQZ) (termed "large") and very good agreement was found throughout. For example, the first dipole moment derivatives with respect to the antisymmetric stretching vibrations of linear C_7 and C_9 as obtained with the two basis sets differ from each other by less than 1%.

The absolute intensities of the IR active fundamentals of either σ_u or π_u symmetry are calculated according to the formula:

$$A_i = \frac{N_A g_i}{12 c_0^{\,2} \epsilon_0}\left[\sum_{j=1}^{n}\left(\frac{\partial \mu_\alpha}{\partial S_j}\right)_e L_{ji}\right]^2 \qquad (1)$$

In eq 1, N_A is Avogadro's number, c_0 the vacuum velocity of light, ϵ_0 is the permittivity of vacuum, and g_i is the degeneracy of the vibration under study (1 for stretching and 2 for bending vibrations). L_{ji} are elements of the **L** matrix which connects the symmetry coordinates with the normal coordinates. When the dipole moment derivatives $(\partial\mu_\alpha/\partial S_j)_e$, where the index α stands for either the parallel or the perpendicular component of the dipole moment vector, the **L** matrix elements and the fundamental physical constants are given in atomic units, the conversion factor to A (in km mol^{-1}) is 1.777×10^6.

For linear carbon chains with more than three atoms, comparison of calculated IR intensities with gas-phase experimental data is so far restricted to linear C_7 and C_9, but because of the lack of precision of the measurements, no thorough examination of the accuracy of the theoretical values is yet possible. In the case of C_7, Heath et al.[24] estimated the ν_5 band to be 5 to 7 times weaker than the ν_4 band. This may be compared with a calculated ratio of 3.34. For linear C_9, experiments by van Orden et al.[25] yielded a relative intensity of 0.11 for the ν_5 band with respect to the more intense ν_6 band. The standard calculations from the present work (CCSD(T)/cc-pVTZ for the harmonic force field and CCSD(T)/small basis for dipole moment derivatives) yield absolute IR intensities of 3299 and 7209 km mol^{-1} for the ν_5 and ν_6 bands, respectively, and thus a relative intensity of 0.46 for the former. For this carbon chain, the experimental band origins of the two stretching vibrations differ by only 65 cm^{-1}, and as some explorative calculations with slightly modified force fields have shown, the intensity ratio reacts rather sensitively. It is thus possible that effects of vibrational anharmonicity may play a larger role in this particular case.

3. Results and Discussion

3.1. Equilibrium Structures, Rotational Constants, and Dipole Moment Derivatives. Equilibrium bond lengths for linear C_{2n+1} species ($n = 6-9$) as calculated by CCSD(T) with the cc-pVTZ basis set are listed in Table 2. For C_{13} and C_{15}, comparison is made with recommended equilibrium structures

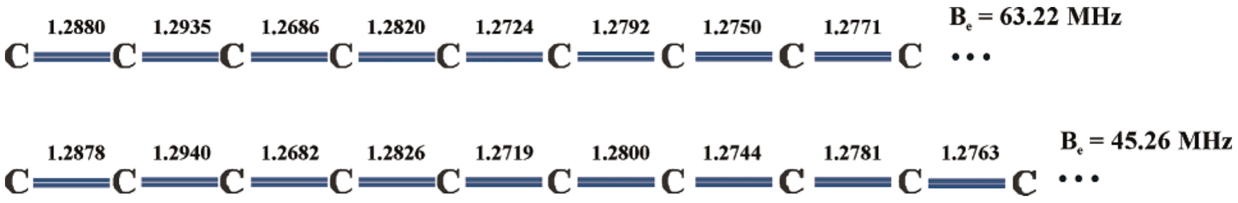

Figure 1. Recommended equilibrium structures and corresponding equilibrium rotational constants for linear C_{17} and C_{19}.

TABLE 3: CCSD(T) Dipole Moment Derivatives (in au or e) with Respect to the Normalized Antisymmetric Stretching Coordinates of Linear C_{2n+1} Chains ($n = 5-9$)[a]

	C_{11}		C_{13}		C_{15}	C_{17}	C_{19}
no.[b]	large[c]	small	large[d]	small	small	small	small
1	3.918	3.939	4.426	4.455	4.943	5.425	5.845
2	−3.893	−3.888	−4.446	−4.444	−4.948	−5.390	−5.777
3	2.872	2.871	3.137	3.145	3.380	3.558	3.707
4	−3.281	−3.247	−3.734	−3.692	−4.079	−4.375	−4.609
5	2.939	2.911	3.099	3.067	3.191	3.236	3.250
6			−3.303	−3.258	−3.541	−3.772	−3.834
7					3.257	3.240	3.108
8						−3.402	−3.368
9							3.121

[a] All calculations are carried out around the recommended equilibrium structures from the present work (cf. Figure 1) and earlier work (refs 13 and 22). [b] Symmetry coordinates are counted from outermost to innermost. [c] 538 cGTOs (ref 14). [d] 630 cGTOs (ref 16).

TABLE 4: CCSD(T) Dipole Moment Derivatives (in au or ea_0) with Respect to the Normalized Cis-Bending Symmetry Coordinates of Linear C_{2n+1} Chains ($n = 5-9$)[a]

	C_{11}		C_{13}		C_{15}	C_{17}	C_{19}
no.[b]	large[c]	small	large[d]	small	small	small	small
1	−0.950	−0.960	−0.978	−0.987	−1.009	−1.026	−1.040
2	−1.689	−1.715	−1.756	−1.784	−1.837	−1.880	−1.917
3	−1.719	−1.745	−1.844	−1.877	−1.977	−2.058	−2.124
4	−2.035	−2.076	−2.217	−2.263	−2.407	−2.524	−2.619
5	−1.367	−1.387	−2.207	−2.244	−2.457	−2.626	−2.764
6			−1.689	−1.721	−2.704	−2.919	−3.095
7					−1.848	−2.901	−3.133
8						−2.155	−3.326
9							−2.300

[a] All calculations are carried out around the recommended equilibrium structures from the present work (cf. Figure 1) and earlier work. [b] Symmetry coordinates are counted from outermost to innermost. [c] 538 cGTOs (ref 14). [d] 630 cGTOs (this work).

TABLE 5: Comparison of CCSD(T)/vtz and CCSD(T)/vqz Harmonic Vibrational Wavenumbers for Linear C_{13}

vibration	vtz	vqz[a]	vibration	vtz	vqz[a]
ω_1 (σ_g)	2190.0	2190.9	ω_7 (σ_u)	2201.8	2204.3
ω_2 (σ_g)	2139.2	2142.9	ω_8 (σ_u)	2030.6	2037.4
ω_3 (σ_g)	1879.3	1889.2	ω_9 (σ_u)	1940.8	1939.5
ω_4 (σ_g)	1433.0	1442.5	ω_{10} (σ_u)	1677.5	1687.8
ω_5 (σ_g)	903.1	909.5	ω_{11} (σ_u)	1174.7	1182.9
ω_6 (σ_g)	314.2	316.4	ω_{12} (σ_u)	617.1	621.3
ω_{13} (π_g)	518.5	508.5	ω_{18} (π_u)	518.7	507.9
ω_{14} (π_g)	471.3	466.5	ω_{19} (π_u)	489.2	485.7
ω_{15} (π_g)	280.2	272.2	ω_{20} (π_u)	430.9	426.2
ω_{16} (π_g)	173.3	168.8	ω_{21} (π_u)	231.1	223.9
ω_{17} (π_g)	61.8	60.9	ω_{22} (π_u)	114.2	111.9
			ω_{23} (π_u)	23.2	23.0

[a] With the exception of the values for vibrations of π_g symmetry, data are taken from the author's earlier papers (refs 13 and 16).

which were previously obtained by applying systematic corrections to the results of CCSD(T) calculations with the larger cc-pVQZ basis set.[13] For the outermost four carbon−carbon distances R_{1e}, R_{2e}, R_{3e}, and R_{4e}, the CCSD(T)/cc-pVTZ values are larger than the corresponding recommended ones by 0.0074 Å, 0.0058−0.0059 Å, 0.0066 Å, and 0.0062 Å, respectively. We will therefore take $\Delta R_{1e} = -0.0074$ Å, $\Delta R_{2e} = -0.0058$ Å, $\Delta R_{3e} = -0.0066$ Å, and $\Delta R_{4e} = -0.0062$ Å as corrections for the four outermost equilibrium bond lengths of the longer chains. From R_{5e} on, the differences appear to be practically constant such that a uniform correction of −0.0064 Å should be appropriate. By applying these five different correction parameters to the CCSD(T)/cc-pVTZ results of Table 2, we arrive at the recommended equilibrium structures of linear C_{17} and C_{19} as displayed in Figure 1. As is typical for cumulenic systems, there is only little variation in the CC equilibrium distances, the difference between largest and smallest value amounting to 0.0249 Å for C_{17} and 0.0258 Å for C_{19}. The figure also lists recommended equilibrium rotational constants B_e which, according to our previous work for the smaller C_{2n+1} chains, should provide quite good approximations to the still unknown experimental ground-state values. The B_e predictions for linear C_{17} and C_{19} from the present work are virtually identical with the author's earlier ones (63.23 and 45.27 MHz[13]), which were obtained by simply extending the recommended equilibrium structure of C_{15} by one or two C_2 links in the center of the molecule with a common distance of $R_e = 1.277$ Å.

CCSD(T) first derivatives of the electric dipole moment with respect to the antisymmetric stretching coordinates are listed in Table 3. The basis sets termed "small" and "large" have been explained in section 2. For linear C_{11} and C_{13}, the differences between results obtained by calculations with the two basis sets are very small (1.4% or less), thereby justifying the use of the "small" basis for the longer carbon chains. As has been discussed in our previous work for linear C_{11} and C_{13},[14,16] electron correlation is of utmost importance to arrive at reliable values for the derivatives. The same situation holds for the longer chains. Since this information is probably of minor interest to the general reader, it is supplied as Supporting Information (cf. Table S3). For the CCSD(T) first dipole moments with respect to the cis-bending symmetry coordinates (cf. Table 4), the differences between the results obtained with the two basis sets are small as well. Actually, they are never extending 2%.

3.2. Harmonic Vibrational Wavenumbers and Absolute IR Intensities. In order to calculate the full set of harmonic vibrational wavenumbers, the complete harmonic (quadratic) force fields (consisting of all second derivatives of the total energy with respect to the symmetry coordinates, taken at equilibrium) are required. Since the total number of quadratic force constants of the five molecules under investigation is rather large, these data are made available as Supporting Information (cf. Tables S1−S2b and S4a−S6b).

CCSD(T)/vtz and CCSD(T)/vqz harmonic vibrational wavenumbers for linear C_{13} are listed in Table 5. While the CCSD(T)/vqz values for the vibrations of σ_g, σ_u, and π_u symmetry have been published earlier,[13,16] those for the five normal vibrations of π_g symmetry have been newly calculated. Not surprisingly, about the same sort of agreement between the

TABLE 6: Harmonic Vibrational Wavenumbers (in cm^{-1}) and IR Intensities (in km mol^{-1}; in Parentheses) for Linear C$_{15}$^{a}

vibration		vibration	
ω_1 (σ_g)	2181.5	ω_8 (σ_u)	2218.7 (3369)
ω_2 (σ_g)	2145.8	ω_9 (σ_u)	2124.3 (1289)
ω_3 (σ_g)	1993.3	ω_{10} (σ_u)	1910.5 (8495)
ω_4 (σ_g)	1698.9	ω_{11} (σ_u)	1861.5 (19,948)
ω_5 (σ_g)	1265.7	ω_{12} (σ_u)	1497.6 (409)
ω_6 (σ_g)	792.2	ω_{13} (σ_u)	1042.5 (20)
ω_7 (σ_g)	272.6	ω_{14} (σ_u)	542.3 (11)
ω_{15} (π_g)	519.0	ω_{21} (π_u)	519.4 (10.7)
ω_{16} (π_g)	480.1	ω_{22} (π_u)	489.9 (4.6)
ω_{17} (π_g)	420.1	ω_{23} (π_u)	458.2 (0.3)
ω_{18} (π_g)	243.3	ω_{24} (π_u)	286.1 (2.8)
ω_{19} (π_g)	139.7	ω_{25} (π_u)	192.8 (12.7)
ω_{20} (π_g)	47.5	ω_{26} (π_u)	89.6 (13.0)
		ω_{27} (π_u)	17.6 (7.9)

[a] From CCSD(T)/cc-pVTZ quadratic force field (see Supporting Information Table S4a,b) and first dipole moment derivatives of Tables 3 and 4.

TABLE 7: Harmonic Vibrational Wavenumbers (in cm^{-1}) and IR Intensities (in km mol^{-1}; in Parentheses) for Linear C$_{17}$^{a}

vibration		vibration	
ω_1 (σ_g)	2196.0	ω_9 (σ_u)	2181.4 (3384)
ω_2 (σ_g)	2102.5	ω_{10} (σ_u)	2151.9 (3865)
ω_3 (σ_g)	2070.9	ω_{11} (σ_u)	1974.0 (784)
ω_4 (σ_g)	1863.0	ω_{12} (σ_u)	1775.1 (28,413)
ω_5 (σ_g)	1525.4	ω_{13} (σ_u)	1706.7 (4963)
ω_6 (σ_g)	1133.1	ω_{14} (σ_u)	1334.0 (236)
ω_7 (σ_g)	704.5	ω_{15} (σ_u)	923.2 (7)
ω_8 (σ_g)	240.8	ω_{16} (σ_u)	476.9 (14)
ω_{17} (π_g)	519.7	ω_{24} (π_u)	519.9 (10.5)
ω_{18} (π_g)	483.6	ω_{25} (π_u)	485.3 (4.6)
ω_{19} (π_g)	447.1	ω_{26} (π_u)	447.0 (0.1)
ω_{20} (π_g)	290.9	ω_{27} (π_u)	359.3 (1.3)
ω_{21} (π_g)	208.2	ω_{28} (π_u)	246.7 (6.5)
ω_{22} (π_g)	113.6	ω_{29} (π_u)	155.3 (13.0)
ω_{23} (π_g)	37.5	ω_{30} (π_u)	69.0 (10.4)
		ω_{31} (π_u)	13.1 (6.6)

[a] From CCSD(T)/cc-pVTZ quadratic force field (see Supporting Information Table S5a,b) and first dipole moment derivatives of Tables 3 and 4.

TABLE 8: Harmonic Vibrational Wavenumbers (in cm^{-1}) and IR Intensities (in km mol^{-1}; in Parentheses) for Linear C$_{19}$^{a}

vibration		vibration	
ω_1 (σ_g)	2194.2	ω_{10} (σ_u)	2177.6 (1533)
ω_2 (σ_g)	2133.3	ω_{11} (σ_u)	2151.0 (7904)
ω_3 (σ_g)	2044.0	ω_{12} (σ_u)	2050.3 (2724)
ω_4 (σ_g)	1955.0	ω_{13} (σ_u)	1857.0 (448)
ω_5 (σ_g)	1722.5	ω_{14} (σ_u)	1680.6 (34,040)
ω_6 (σ_g)	1387.6	ω_{15} (σ_u)	1553.5 (1304)
ω_7 (σ_g)	1025.2	ω_{16} (σ_u)	1209.1 (127)
ω_8 (σ_g)	634.1	ω_{17} (σ_u)	832.4 (1)
ω_9 (σ_g)	215.6	ω_{18} (σ_u)	428.4 (16)
ω_{19} (π_g)	520.4	ω_{27} (π_u)	520.8 (11.2)
ω_{20} (π_g)	486.2	ω_{28} (π_u)	495.5 (4.5)
ω_{21} (π_g)	461.5	ω_{29} (π_u)	476.3 (0.3)
ω_{22} (π_g)	405.1	ω_{30} (π_u)	438.0 (0.2)
ω_{23} (π_g)	260.3	ω_{31} (π_u)	295.1 (1.7)
ω_{24} (π_g)	177.6	ω_{32} (π_u)	220.7 (9.1)
ω_{25} (π_g)	93.6	ω_{33} (π_u)	134.2 (11.5)
ω_{26} (π_g)	30.3	ω_{34} (π_u)	58.3 (9.5)
		ω_{35} (π_u)	11.1 (5.9)

[a] From CCSD(T)/cc-pVTZ quadratic force field (see Supporting Information Table S6a,b) and first dipole moment derivatives of Tables 3 and 4.

values obtained with the two basis sets was achieved as for linear C$_{11}$ (cf. Table 1). In particular, the CCSD(T)/vtz values for the harmonic wavenumbers of the antisymmetric stretching vibrations of σ_u symmetry differ from their CCSD(T)/vqz counterparts by no more than 10.3 cm^{-1}. Likewise, the absolute IR intensities from the "standard level" of the present work (CCSD(T) with vtz basis for force field and "small" basis for dipole moment derivatives) are in very good agreement with the author's previous values from more extensive calculations.[13,16] For example, the difference in the intensity of the strongest vibration of linear C$_{13}$ (ν_9) amounts to only 1.9%.

Results of calculations at the "standard level" for linear C$_{15}$, C$_{17}$, and C$_{19}$ are listed in Tables 6−8. The most intense vibration of linear C$_{15}$ is predicted to be the antisymmetric stretching vibration ν_{11} (see Table 6), for which a large absolute IR intensity of 19 948 km mol^{-1} has been obtained. The corresponding harmonic wavenumber is calculated to be 1861.5 cm^{-1}. It may be compared with the experimental anharmonic values of 1686.8 and 1694.7 cm^{-1}, measured by IR spectroscopy in Ne and Ar matrixes, respectively.[7,26] The differences between theoretical and experimental values of 166.8 and 174.7 cm^{-1} may appear to be rather large. However, already a value of 131.8 cm^{-1} was obtained for the difference ω_9 (CCSD(T)/vtz) − ν_9 (exptl) of linear C$_{13}$, where the accurate experimental gas-phase value of 1808.96 cm^{-1} is employed for ν_9 (exptl).[2] It is currently unclear, whether unusually large effects of vibrational anharmonicity or limitations of the CCSD(T) method provide the major contribution to this difference.

Among the IR active stretching vibrations of linear C$_{17}$ (cf. Table 7), the ν_{12} band with a calculated harmonic wavenumber of 1775 cm^{-1} is predicted to be the most intense vibration. Experimental values by Krätschmer and co-workers are 1548.1 cm^{-1} (Ne matrix) and 1573 cm^{-1} (Ar matrix).[7,26] For linear C$_{19}$, the CCSD(T)/vtz harmonic wavenumber of the strongest vibration goes down to 1681 cm^{-1}, and the absolute IR intensity rises to 34 040 km mol^{-1} (see Table 8). Experimental data from Krätschmer and co-worker's laboratory are 1391 cm^{-1} (Ne matrix) and 1446.3 cm^{-1} (Ar matrix).[7,26]

In order to get some information on the flexibility of linear C$_{17}$ and C$_{19}$ with respect to bending away from linearity, various one-dimensional potential curves have been computed over a larger range of angular distortions. The results are graphically displayed in Figures 2−4; explicit energy values are quoted in Tables S7−S9 (Supporting Information). Throughout, all potential curves are rather steep and of almost parabolic shape, providing some indication that the harmonic approximation should work reasonably well for the bending vibrations of these carbon chains. Figure 2 shows seven cis-bending and seven trans-bending curves for linear C$_{17}$; the remaining curve for bending about the central carbon atom is shown in Figure 4 together with the corresponding results for C$_3$ and C$_{19}$. As is obvious from Figure 2 (see also diagonal quadratic force constants of Table S5b), six of the seven pairs of (cis, trans) bending potentials are almost identical. Only the cis- and trans-bending potentials involving the innermost two equivalent angles (termed θ_7 and θ_7') show a significant difference, with the trans-bending potential being the steeper one. A similar situation was observed for linear C$_{11}$ (cf. Figure 1 of ref 14). Figure 3 shows those cis-bending potentials for linear C$_{19}$ which correspond to symmetry coordinates S_{27}−S_{34}, with S_{35} denoting the symmetry coordinate for central CCC bending (cf. Figure 4). In the order of decreasing steepness, the cis-bending curves for linear C$_{19}$ correspond to symmetry coordinates S_{28}, S_{30}, S_{32}, S_{34}, S_{33}, S_{31}, S_{29}, and S_{27}, with the last coordinate involving the outermost

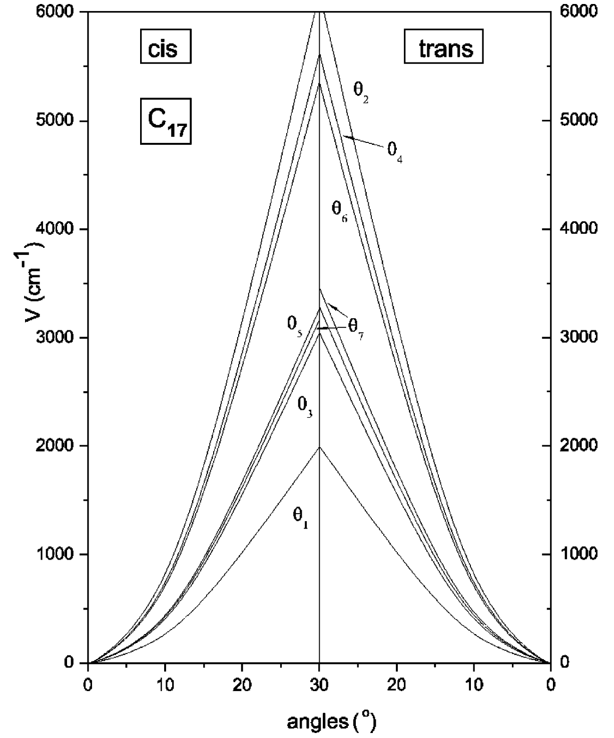

Figure 2. Dependence of potential energy V of linear C_{17} on bending coordinates, with angles $\theta_1-\theta_7$ counted from outermost to innermost. Throughout, two equivalent angles are changed simultaneously by the same amount to produce either a cis-like or a trans-like nuclear configuration. For variation of V with the central CCC angle, see Figure 4.

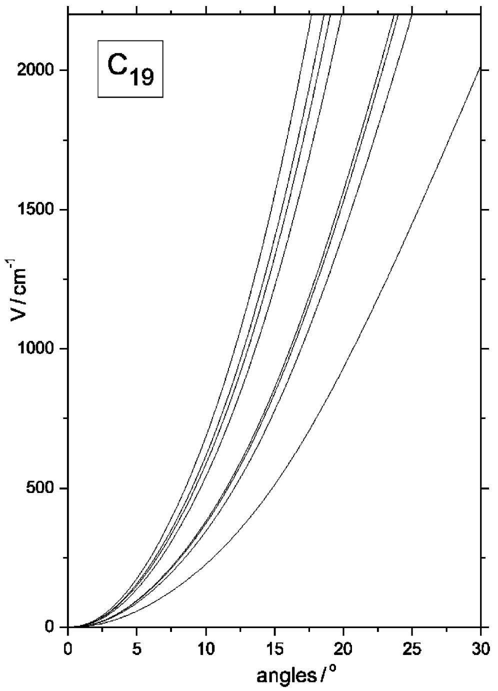

Figure 3. Dependence of potential energy V of linear C_{19} with cis-bending angles, analogous to left-hand side of Figure 2. See the text for the assignment of the individual curves. For variation of V with the central CCC angle, see Figure 4.

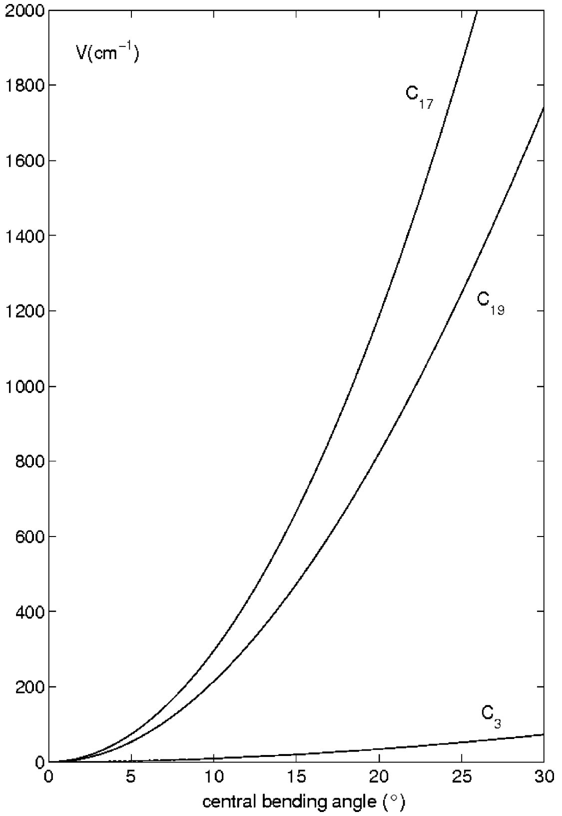

Figure 4. Comparison of CCSD(T)/vtz potentials of linear C_3, C_{17}, and C_{19} for bending about the central carbon atom.

equivalent angles θ_1 and θ_1'. The curves showing the dependence of the potential energy on the central CCC angle for the carbon chains C_3, C_{17}, and C_{19} (see Figure 4) are in line with the expectations from our previous theoretical work.[13,14] The differences between the potential curves for C_{17} and C_{19} are significantly smaller than those for C_{13} and C_{15} (cf. Figure 2 of ref 14). In comparison, the corresponding curve for C_3 is way down. Actually, the potential curve obtained by CCSD(T)/vtz is considerably steeper than that calculated by CCSD(T)/vqz, the relative energies at an angle of 30° amounting to 72.6 and 40.4 cm^{-1}, respectively. In conclusion, the smaller cc-pVTZ basis does quite a good job for C_{2n+1} chains with $n \geq 2$ but is not appropriate for a quantitative description of C_3 (cf. ref 8 for a discussion of the basis set dependence).

Already for linear C_{11} (see Table 1), the CCSD(T)/vtz harmonic wavenumbers of the first vibrations in π_g and π_u symmetries (ω_{11} and ω_{15}, respectively) are almost identical, and this situation continues for the longer chains (see Tables 5−8). On the other hand, earlier quantum-chemical calculations with the smaller cc-pVDZ basis for linear C_{11} and C_{13} strongly overestimate the difference.[27,28] Irrespective of the method employed (SCF, CASSCF, or B3LYP), the difference in calculated harmonic wavenumbers ranges between 77 and 93 cm^{-1} for C_{11} and between 71 and 93 cm^{-1} for C_{13}. As was pointed out earlier by the author,[13] calculations with the cc-pVDZ basis set yield values for the highest vibration of π_u symmetry which are too large by up to approximately 300 cm^{-1}. For the IR active bending vibrations of lowest wavenumber, which are of greatest interest to forthcoming far-infrared astronomy, the differences between CCSD(T)/vqz and CCSD(T)/vtz results, currently available for linear C_{11} and C_{13} (cf. Tables 1 and 5), are only 0.4 cm^{-1} or less. Since there are no clear indications for large anharmonicity effects on the bending vibrations, the predictions from the present work for linear C_{17} and C_{19} should have almost the same quality as those for C_{13} and C_{15} from the author's earlier work.[15]

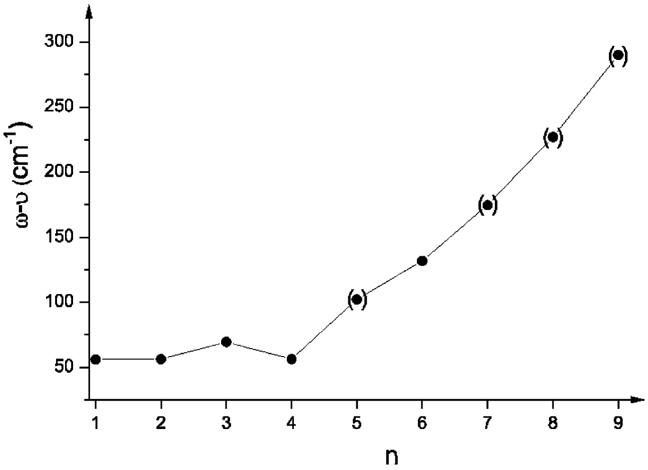

Figure 5. Differences between CCSD(T)/vtz harmonic wavenumbers and corresponding anharmonic experimental values (neon matrix data in parentheses) for most intense antisymmetric stretching vibrations of C_{2n+1} chains.

4. Conclusions

In agreement with the interpretation of experiments by Krätschmer and co-workers,[7,26] which may still be somewhat tentative, the calculations of the present work predict one vibrational band to carry the major part of the total IR intensity of the cumulenic carbon chains C_{15}, C_{17}, and C_{19}. Adopting the conventional spectroscopic numbering of molecular vibrations for linear molecules, these are ν_{11} (C_{15}), ν_{12} (C_{17}), and ν_{14} (C_{19}). Within the double-harmonic approximation, the absolute intensity of the last mentioned band is calculated to be as high as 34 040 km mol^{-1}. Although the calculations of the present work may well be considered to be of current state-of-the-art quality, the author feels himself unable to make a realistic estimate of the error of that value. A still higher value of 60 974 km mol^{-1}, obtained by B3LYP calculations with the small 6-311G(d) basis set,[7] appears to be too large. The PM3 value of 357 293 km mol^{-1} published by the same authors[7] is considered to be completely unrealistic. The big differences between CCSD(T)/vtz harmonic wavenumbers and the corresponding experimental (mostly neon matrix) anharmonic values for the most intense vibrations of the longer carbon chains (see Figure 5) are still puzzling. Clearly, further theoretical and experimental studies are required in order to solve this problem.

The present work should have demonstrated that Dunning's cc-pVTZ basis set already does quite a good job for carbon chains of type C_{2n+1}, with $n = 1$, that is, quasi-linear C_3, being a serious exception. In particular, the predictions made for the IR active bending vibrations occurring in the far-infrared region of the electromagnetic spectrum are expected to be of sufficiently high accuracy to assist experimentalists in the search for the corresponding spectra and, hopefully, also astronomers in their attempts to unambiguously detect carbon chains larger than C_5.

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Supporting Information Available: Quadratic force constants, first derivatives, total energies, and relative energies for linear carbon chains. This material is available free of charge via the Internet at http://pubs.acs.org.

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