Theor Chem Acc (2005) 114: 350–356
DOI 10.1007/s00214-005-0690-8

REGULAR ARTICLE

Peter Botschwina

On the equilibrium structures and the IR active bending vibrations of linear C_{13} and C_{15}: results of large-scale coupled cluster calculations

Received: 15 July 2005 / Accepted: 19 July 2005 / Published online: 23 September 2005

Abstract Accurate equilibrium (r_e) structures (ca. 0.0005 Å accuracy in bond lengths) have been established for linear C_{13} and C_{15} by applying a uniform correction to the results of CCSD(T) calculations with the cc-pVQZ basis set. The equilibrium bond lengths cover a small range between 1.2690 and 1.2928 Å and are indicative of strong carbon–carbon double bonds. Equilibrium structures of still longer chains may be obtained by taking the recommended r_e structure for C_{15} and inserting one or more C_2 links with R_e = 1.277 Å in the middle of the molecule. Both linear C_{13} and C_{15} exhibit no sign of floppiness and appear to behave like fairly normal semi-rigid molecules. Diagonal potentials for the IR active bending vibrations of both molecules have large correlation contributions between -33 and 47%, with MP2 strongly overshooting with respect to CCSD(T). Harmonic *cis*-bending vibrational wavenumbers and their absolute IR intensities are predicted. Since the latter are rather small, the chances of an interstellar detection of linear C_{13} or C_{15} in the far IR may be poor.

Keywords Carbon chains · Coupled cluster · Equilibrium structures · Bending vibrations · IR intensities

1 Introduction

Linear carbon chains are of considerable interest to the chemistry of combustion and astrochemistry (see [1, 2] for reviews). Since they have no permanent electric dipole moment, radio astronomy does not provide the appropriate technique to observe such species in the interstellar medium (ISM) or the circumstellar medium (CSM). However, astronomical observations of the first members of pure carbon chains in the infrared (IR) and visible region of the spectrum have been successful. C_3, which has a linear equilibrium structure and a very shallow bending potential (see, e.g., [3]), has been observed in the circumstellar envelope of the evolved carbon star IRC+10216 through its antisymmetric stretching vibration (ν_3) [4]. Through its bending vibrational transition (ν_2) in the far infrared (FIR) region at ca. 65 cm^{-1}, C_3 was found in the same astronomical source as well as in the direction of Sagittarius B2, making use of either the Infrared Space [5] or the Kuiper Airborne Observatory [6]. Rovibronic transitions of C_3 near 4050 Å have been known to astronomers since its detection in cometary tails as early as in 1881 [7]. The molecule was also observed in the same wavelength region in the atmosphere of cool stars (see [8] for a review) and even in the diffuse ISM [9, 10]. While the interstellar detection of linear C_4 must be considered to be tentative [11], linear C_5 was definitely observed in IRC+10216 through its antisymmetric stretching vibration of highest wavenumber, termed ν_3 [12].

There is an ongoing debate whether longer carbon chains will have bending vibrational transitions with sufficiently large intensities such that satellite-based observation of spectra in the FIR might be possible. It is a major goal of this paper to address this question. Linear C_{13} and C_{15} have been selected for this purpose. For the former species, high-resolution mid-IR spectra have been published [13, 14]. However, no reliable gas-phase spectroscopic information is yet available for the bending vibrations of either linear C_{13} or C_{15}.

Previous quantum-chemical studies of spectroscopic properties for linear C_{13} are of rather unknown reliability, in particular with respect to the calculated wavenumbers and intensities of the IR active bending vibrations. In 1994, SCF calculations with the small 6–31G* basis set were published by Bleil et al. [15]. The results of SCF, CASSCF (8/8) and DFT/B3LYP calculations for harmonic vibrational wavenumbers and IR intensities as obtained within the double harmonic (DH) approximation were reported by Martin and Taylor [16] and Martin et al. [17]. Dunning's cc-pVDZ basis [18], which comprises 182 contracted Gaussian-type orbitals (cGTOs), was employed in these calculations.

Dedicated to Prof. Dr. H. Stoll on the occasion of his 60th birthday.

P. Botschwina
Institut für Physikalische Chemie, Universität Göttingen,
Tammannstraße 6, 37077 Göttingen, Germany
Tel.: +49-551-393133, Fax: +49-551-393144,
E-mail: pbotsch@gwdg.de

Table 1 Parameters (in a.u.) of near-equilibrium *cis*-bending potential energy functions for linear C_{13}^{a}

Term	SCF vqz	MP2 vqz	CCSD vqz	CCSD(T) vqz	CCSD(T) vtz
S_1^2	0.011639	0.024119	0.013343	0.015355	0.016796
S_1^4	−0.000537	−0.001515	−0.000553	−0.000139	−0.002897
S_2^2	0.072830	0.044373	0.057690	0.050543	0.052885
S_2^4	0.001088	−0.000391	0.000750	0.000471	−0.004609
S_3^2	0.016458	0.034133	0.020326	0.024128	0.025725
S_3^4	−0.000420	−0.001551	−0.000137	−0.000285	−0.003651
S_4^2	0.069989	0.039075	0.054573	0.047221	0.048299
S_4^4	0.000017	−0.001644	0.000075	−0.000139	−0.002105
S_5^2	0.017519	0.035665	0.021050	0.024752	0.025926
S_5^4	−0.001689	−0.003627	−0.001581	−0.001718	−0.003523
S_6^2	0.068848	0.037413	0.053423	0.046053	0.047114
S_6^4	0.001922	0.000134	0.002380	0.002263	−0.001959
S_1S_2	0.005557	0.001609	0.002232	0.001922	0.001393
S_1S_3	−0.001231	−0.002150	−0.001444	−0.001453	−0.002083
S_1S_4	−0.000330	−0.000082	−0.000066	0.000042	0.000094
S_1S_5	−0.000064	−0.000066	−0.000033	0.000009	−0.000066
S_1S_6	−0.000028	−0.000104	−0.000058	−0.000067	−0.000005
S_2S_3	0.014234	0.013739	0.013230	0.013768	0.014107
S_2S_4	−0.008032	−0.005893	−0.007091	−0.006157	−0.006232
S_2S_5	−0.001155	−0.001149	−0.001083	−0.001002	−0.001658
S_2S_6	0.000671	0.000395	0.000592	0.000568	0.000486
S_3S_4	0.011780	0.011473	0.011063	0.011909	0.011918
S_3S_5	−0.001459	−0.002971	−0.001953	−0.002079	−0.002494
S_3S_6	−0.001297	−0.001486	−0.001335	−0.001261	−0.001579
S_4S_5	0.012778	0.012425	0.011949	0.012733	0.012922
S_4S_6	−0.011335	−0.007730	−0.009796	−0.008285	−0.008645
S_5S_6	0.018375	0.018280	0.017398	0.018597	0.018824

[a] See Eq. (1a–2) for the definition of symmetry coordinates and PEF terms. All calculations are carried out around the CCSD(T)/cc-pVQZ equilibrium structure

2 Details of calculations and results

Like in the author's previous work on closed-shell carbon chains [19–22], the coupled cluster variant CCSD(T) [23] is employed as the most sophisticated ab initio method of the present study. For comparison, various results obtained by HF-SCF, MP2 and CCSD will be quoted as well. Most of the present calculations make use of Dunning's cc-pVQZ basis set [18], which involves 55 cGTOs per carbon atom. Such calculations for C_{13} and C_{15} thus comprise 715 and 825 cGTOs, respectively. As has been shown earlier for C_3 [3], a basis set of this size may be mandatory to obtain accurate results for shallow CCC bending potentials. Throughout, valence electrons are correlated in the post-Hartree-Fock calculations. All electronic structure calculations of the present work were carried out with the MOLPRO suite of programmes [24–26].

Calculated equilibrium structures for linear C_{13} and C_{15} as obtained by the four different ab initio methods noted above are displayed in Fig. 1. The figure also includes recommended equilibrium bond lengths which were derived from the CCSD(T) values by subtracting a uniform correction of 0.0037 Å as established earlier (see [22] and references therein). It mainly corrects for the neglect of core–valence and core–core correlation, but should also account for smaller errors arising from basis set incompleteness and the approximations made in CCSD(T), i.e., neglect of connected quadruple and higher substitutions and non-iterative treatment of connected triples. The resulting recommended equilibrium (r_e) structure for C_{13} agrees closely (maximum difference: 0.0006 Å) with the author's previous work [22], which involved CCSD(T) calculations with the smaller cc-pVTZ basis set [18]. The equilibrium rotational constant as obtained from the recommended r_e structure of the present work is B_e=141.66 MHz, to be compared with the author's previous value of 141.69 MHz [22] and the experimental ground-state rotational constant of B_0=141.87(2) MHz [13], where the standard deviation in terms of the least significant digit is given in parentheses.

The lower part of Fig. 1 summarizes the results obtained for linear C_{15}. Upon comparison with those calculated for C_{13}, no great differences are observed. Again, as emphasized in the author's previous work on linear C_{11} [22], connected triple substitutions provide non-negligible and non-uniform contributions to the individual carbon–carbon equilibrium bond lengths. Like for C_{13} and C_{11}, the MP2 results are surprisingly close to those obtained by CCSD(T), the maximum deviation not exceeding 0.0033 Å. However, this must be considered to be a result of fortuitous error cancellation since

Table 2 Diagonal part of *cis*-bending potential energy functions for linear C_{15}^{a}

Term	SCF vqz	MP2 vqz	CCSD vqz	CCSD(T) vqz	CCSD(T) vtz
S_1^2	0.011885	0.024594	0.013601	0.015608	0.017145
S_1^4	−0.000687	−0.001167	−0.000600	−0.000145	−0.003173
S_2^2	0.072641	0.043681	0.057438	0.050239	0.052717
S_2^4	0.001025	−0.000097	0.000740	0.000603	−0.004957
S_3^2	0.016765	0.035128	0.020703	0.024503	0.026068
S_3^4	−0.000456	−0.001710	−0.000327	−0.000370	−0.003027
S_4^2	0.069293	0.037528	0.053784	0.046380	0.047593
S_4^4	0.000396	−0.001110	0.000575	0.000456	−0.002231
S_5^2	0.018769	0.038736	0.022605	0.026399	0.027818
S_5^4	−0.001231	−0.002093	−0.000514	−0.000453	−0.004209
S_6^2	0.063944	0.032536	0.048967	0.042111	0.043167
S_6^4	−0.002718	−0.003847	−0.002371	−0.001946	−0.003353
S_7^2	0.019436	0.040001	0.023272	0.027004	0.028038
S_7^4	−0.000840	−0.002423	0.000261	0.000427	−0.003708

[a] See Eq. (1a–2) for the definition of symmetry coordinates and PEF terms. All calculations are carried out around the CCSD(T)/cc-pVQZ equilibrium structure. All values in a.u.

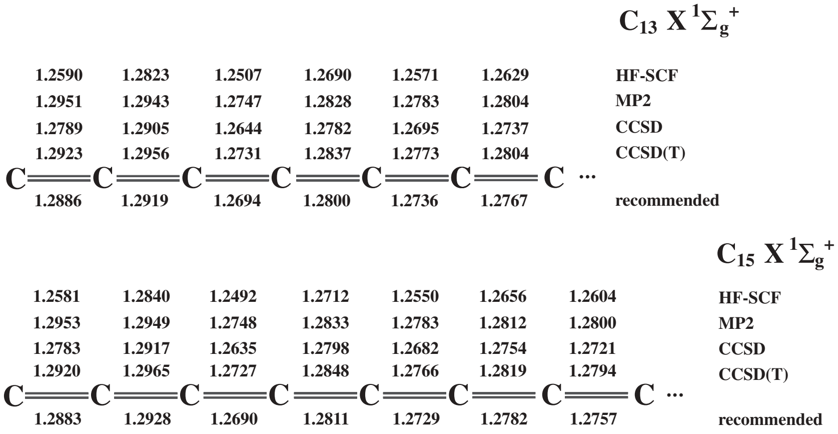

Fig. 1 Ab initio (basis set: cc-pVQZ) and recommended equilibrium bond lengths (in Å) for linear C_{13} and C_{15}

MP2 takes only double substitutions explicitly into account. From the recommended r_e structure, $B_e(C_{15}) = 92.11$ MHz is obtained. The corresponding ground-state value is predicted as B_0=92.2(1) MHz, where the estimated error in terms of the least significant digit is given in parentheses.

Figure 2 graphically displays the recommended equilibrium bond lengths for linear C_{15} in an analogous way as done earlier for linear C_{14} [22]. Again, oscillatory behavior is observed and the innermost CC equilibrium bond lengths are approaching a constant value of 1.277 Å. An almost identical value of 1.276 Å was obtained for the C_{2n} series with $^3\sum_g^-$ ground states [22]. We may therefore predict equilibrium structures of still larger carbon chains of type C_{2n+1} with reasonable accuracy by starting with the recommended r_e structure for C_{15} and inserting one or more C_2 links with $R_e = 1.277$ Å in the middle of the molecule. B_e predictions for linear C_{17} and C_{19} obtained in this way are 63.23 and 45.27 MHz, respectively. The corresponding B_0 values are expected to be only slightly larger.

In order to describe the IR active bending vibrations of C_{2n+1} chains, which are of π_u symmetry and lead to *cis*-like distortions of the nuclear framework out of the equilibrium structure of $D_{\infty h}$ symmetry, we make use of normalized symmetry coordinates. They are defined as

$$S_i = \frac{1}{\sqrt{2}}\left(\Delta\alpha_i + \Delta\alpha_i'\right) \quad i = 1, 2, \ldots, n-1 \tag{1a}$$

$$S_n = \Delta\beta \quad (\beta: \text{ central CCC angle}) \tag{1b}$$

The integer n may also be interpreted as the number of pairwise equivalent bonds. In the present work, these are counted from outermost to innermost and the angular symmetry coordinates accordingly. Near-equilibrium analytical potential energy functions (PEFs) for the *cis*-bending vibrations of linear C_{13} and C_{15} are obtained from ab initio calculations around the CCSD(T)/cc-pVQZ equilibrium structures using distortions of 1°, 5° and 10° for diagonal cuts and additionally pairwise (1°, 1°) distortions in order to determine the quadratic coupling terms. The resulting analytical PEFs as obtained by

Table 3 CCSD(T)/cc-pVTZ quadratic coupling terms (in a.u.) for linear C_{15}^{a}

Term	Value (a.u.)	Term	Value (a.u.)
S_1S_2	0.001301	S_3S_4	0.011769
S_1S_3	−0.002132	S_3S_5	−0.002367
S_1S_4	0.000069	S_3S_6	−0.001293
S_1S_5	0.000049	S_3S_7	−0.000164
S_1S_6	−0.000056	S_4S_5	0.014337
S_1S_7	−0.000100	S_4S_6	−0.005770
S_2S_3	0.014358	S_4S_7	−0.001889
S_2S_4	−0.006087	S_5S_6	0.011647
S_2S_5	−0.001914	S_5S_7	−0.003618
S_2S_6	0.000405	S_6S_7	0.019578
S_2S_7	−0.000106		

[a] See Eq. (1a–2) for the definition of symmetry coordinates and PEF terms. Calculations are carried out around the CCSD(T)/cc-pVQZ equilibrium structure

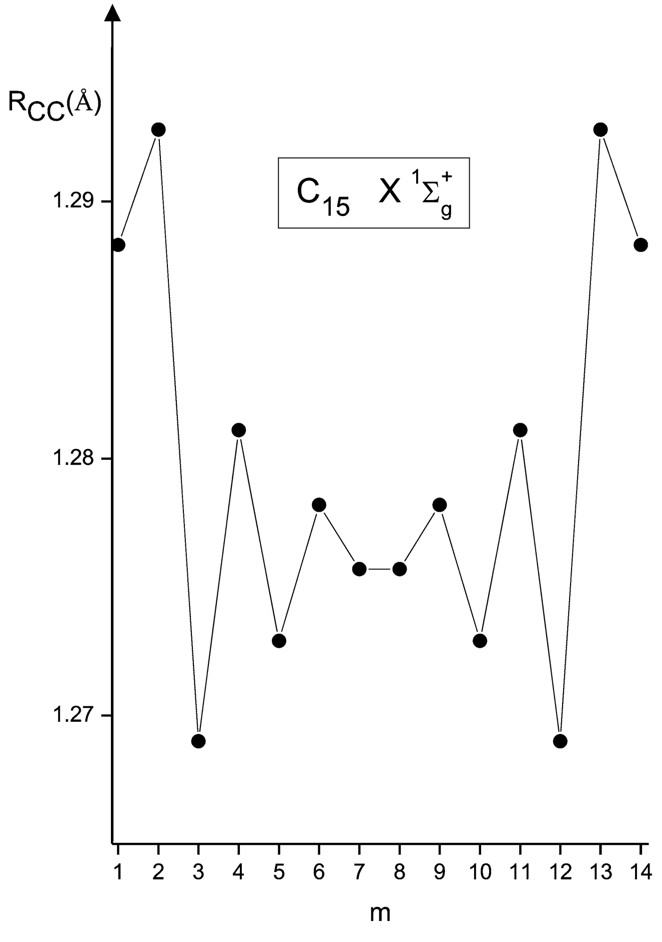

Fig. 2 Comparison of recommended equilibrium bond lengths for linear C_{15}. The index *m* counts the CC bonds, starting with the outermost bond

least-squares fitting have the form

$$V - V_{\mathrm{ref}} = \sum_{i=1}^{n} (C_i^{(2)} S_i^2 + C_i^{(4)} S_i^4) + \sum_{i<j}^{n} C_{ij} S_i S_j \tag{2}$$

The PEF parameters calculated for linear C_{13} are listed in Table 1. The diagonal PEF part is dominated by the quadratic terms, with the quartic terms being rather insignificant for angular distortions of less than 10°. Electron correlation plays an important role. At the CCSD(T)/cc-pVQZ level, the S_i^2 terms exhibit alternating correlation contributions between -33 and 47%. Connected triple substitutions also provide alternating contributions between -14 and 18%, when taken with respect to the corresponding CCSD(T) values. MP2 strongly overestimates the correlation effects on all six S_i^2 terms, most significantly for the S_1^2, S_3^2 and S_5^2 terms which are larger than the corresponding CCSD(T) values by 57, 42 and 44%, respectively. Among the off-diagonal quadratic terms, those involving the coordinate pairs S_2S_3, S_3S_4, S_4S_5 and S_5S_6 play the largest role. The differences between the results obtained by the four different methods are rather small for these terms. The next most important coupling term, involving the combination S_4S_6, shows significantly larger differences. Reduction of the basis set from cc-pVQZ to cc-pVTZ has little effect on the largest coupling terms. The maximum difference of 0.000656 a.u. occurs for the S_2S_5 term; this is only 4% of the largest coupling term (S_5S_6), however.

The parameters of the *cis*-bending PEFs calculated for linear C_{15} are listed in Tables 2 (diagonal part) and 3 (quadratic coupling terms). For economical reasons, the coupling terms were only calculated with the smaller cc-pVTZ basis set (450 cGTOs). On the whole, the situation is quite similar to that discussed for C_{13} and the results of the present work should be transferable to still larger carbon chains.

In previous papers from the Saykally group [2,27,28], the potential for bending around the central carbon atom has been considered to be a measure of the degree of floppiness of a C_{2n+1} species. While spectroscopists have no means to directly get such information, theory is in an easy position to do so. CCSD(T)/cc-pVQZ bending potential curves for bending around the central carbon atom with carbon-carbon distances fixed at their equilibrium values are displayed in Fig. 3 for linear C_{15}, C_{13} and C_3. Like in the previous comparison of C_{2n+1} species with n=1–5 (cf. Fig. 2 of Ref. [20] and Fig. 2 of Ref. [29]) one clearly sees that C_3 is the exception while C_{13} and C_{15} have steep and almost quadratic bending potentials.

Absolute IR intensities for the *cis*-bending vibrations of linear C_{13} and C_{15} have been calculated within the familiar double-harmonic approximation which requires the knowledge of the harmonic vibrations and the first dipole moment

Table 4 First dipole moment derivatives (in a.u.) for linear C_{13} and C_{15} with respect to normalized π_u symmetry coordinates[a]

	C_{13}				C_{15}			
	SCF	MP2	CCSD	CCSD(T)	SCF	MP2	CCSD	CCSD(T)
S_1	−0.565	−1.161	−0.834	−0.944	−0.586	−1.177	−0.855	−0.960
S_2	−1.696	−1.865	−1.788	−1.767	−1.747	−1.911	−1.840	−1.814
S_3	−1.464	−2.149	−1.768	−1.835	−1.563	−2.240	−1.879	−1.939
S_4	−2.120	−2.340	−1.986	−2.213	−2.261	−2.466	−2.403	−2.341
S_5	−1.811	−2.533	−2.142	−2.190	−2.029	−2.756	−2.371	−2.396
S_6	−1.612	−1.775	−1.719	−1.686	−2.545	−2.784	−2.719	−2.647
S_7					−1.538	−2.064	−1.789	−1.801

[a] Throughout, the recommended equilibrium structures (cf. Fig. 1) are taken as reference structures in the calculation of dipole moment derivatives which make use of the avtz' basis (sp(avtz) + df(vtz))

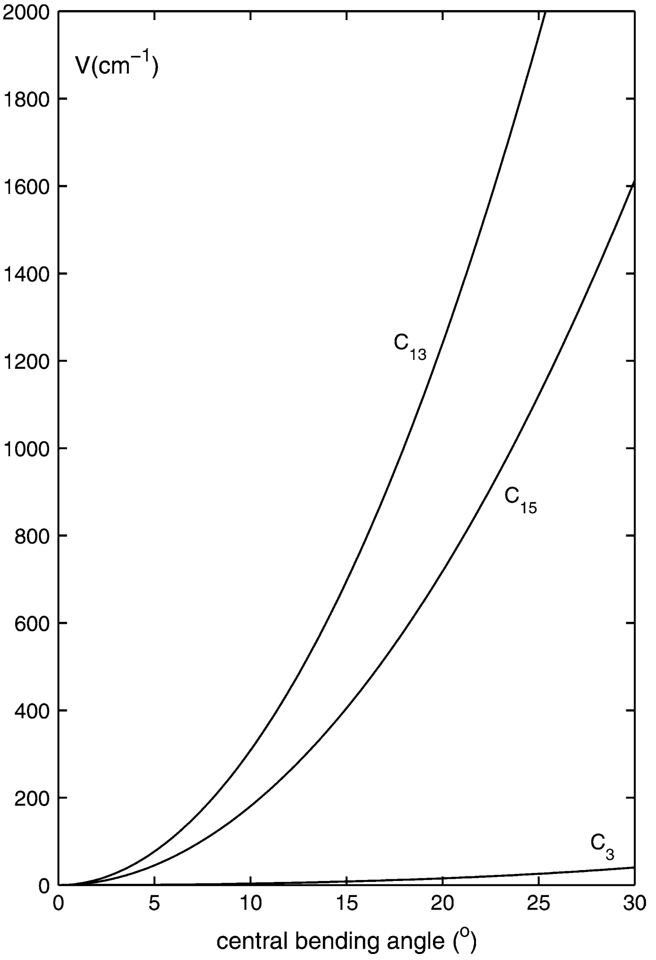

Fig. 3 Comparison of CCSD(T)/cc-pVQZ potentials of linear C_{15}, C_{13} and C_3 for bending about the central carbon atom (bond lengths and other angles kept fixed at their equilibrium values)

derivatives. For the post-Hartree-Fock methods employed in the present work, which do not obey the Hellmann–Feynman theorem, the correlation contributions to the electric dipole moment were calculated as numerical derivatives of the correlation energies with respect to the strength of a uniform electric field, with ±0.0001 a.u. being taken in the actual calculations. Basis sets of 442 and 510 cGTOs were employed for linear C_{13} and C_{15}, respectively. They correspond to extensions of Dunning's cc-pVTZ set [18] by the diffuse *s* and *p* functions from the aug-cc-pVTZ set [30].

Computed first dipole moment derivatives with respect to the *cis*-bending symmetry coordinates S_i ($i = 1$–n) for both carbon chains are listed in Table 4. Upon bending the terminal carbon atoms away from linearity by a given small angle produces the smallest change in the dipole moment among the *n* symmetry coordinates. The corresponding correlation contribution is as large as 67% for C_{13} and 64% for C_{15}. Compared with CCSD(T), MP2 always overestimates the correlation contributions. For some of the symmetry coordinates, these are rather small on a percentage scale, however.

The absolute IR intensities of the *n* *cis*-bending vibrations were calculated according to the formula:

$$A_i = \frac{N_A\, g_i}{12 c_0^2\, \epsilon_0} \left[\sum_{j=1}^{n} \left(\frac{\partial \mu_\perp}{\partial S_j} \right)_e L_{ji} \right]^2 \qquad (3)$$

In Eq. (3), N_A is Avogadro's number, c_0 the vacuum velocity of light, ϵ_0 the permittivity of vacuum and g_i the degeneracy of the vibration under study (2 in the present case). L_{ij} are elements of the L matrix which connects the symmetry coordinates with the normal coordinates. When the dipole moment derivatives $(\partial\mu_\perp/\partial S_j)_e$, the L matrix elements and the fundamental physical constants are given in atomic units, the conversion factor to A (in km mol^{-1}) is $1.777 \cdot 10^6$.

Results for the *cis*-bending vibrations of linear C_{13} are listed in Table 5. The harmonic bending vibration with highest wavenumber, termed ω_{18}, is predicted at 508 cm^{-1}, to be compared with the author's previous CCSD(T)/cc-pVQZ values for C_5 [21] and C_7 [20] of 544.1 and 528.6 cm^{-1}, respectively. The previous calculations by Martin and Taylor [16] and Martin et al. [17] grossly overestimate ω_{18} (C_{13}). Poor agreement with the present work is also observed for ω_{19}. The harmonic wavenumbers from the present CCSD(T) calculations should be accurate to ca. 1% (cf. [21] for the quality of such calculations). Since no large anharmonicity effects are expected, they should also provide good estimates for the corresponding anharmonic values. The lowest vibrational transition of linear C_{13} is predicted at 23 cm^{-1}, with an absolute IR intensity of 9 km mol^{-1}. Despite of the failure of the previous work for the bending vibrations with higher wavenumber, agreement among the four different calculations for the vibration with lowest wavenumber is quite good.

Table 5 Harmonic wavenumbers (in cm^{-1}) and IR intensities (in km mol^{-1}; in parentheses) for IR active bending vibrations of linear C_{13}

	SCF/vdz[a] [16]	CASSCF/vdz[a] [16]	B3LYP/vdz[a] [17]	CCSD(T) this work
ω_{18}	804(142)	793(92)	818(18)	508(14.1)
ω_{19}	656(12)	649(18)	633(0)	486(3.4)
ω_{20}	534(0)	511(0)	472(1)	426(6.6)
ω_{21}	239(4)	244(4)	263(12)	224(9.2)
ω_{22}	119(8)	124(6)	125(14)	112(14.7)
ω_{23}	25(8)	27(10)	25(8)	23(9.1)

[a] Published intensities [16, 17] have been multiplied by a factor of 2 in order to be consistent with the results of the present work (cf. Eq. (3))

Table 6 CCSD(T) harmonic wavenumbers and IR intensities for π_u vibrations of linear C_{15}

No.	ω (cm^{-1})	A (km mol^{-1})
21	506	12.6
22	483	4.2
23	453	0.0
24	281	1.9
25	188	11.3
26	88	12.5
27	17	7.6

Combining the CCSD(T)/cc-pVQZ diagonal quadratic PEF terms with the off-diagonal terms as calculated with the smaller cc-pVTZ basis set leads to changes in the harmonic wavenumbers of less than 3 cm^{-1}. In particular, the differences in the lowest two wavenumbers (ω_{22} and ω_{23}) are only 0.2 and 0.1 cm^{-1}, respectively.

CCSD(T) results for linear C_{15} are reported in Table 6. The wavenumber of the highest *cis*-bending vibration (ω_{21}) differs from the corresponding value for C_{13} by only 1.4 cm^{-1}. With increasing chain length, there appears to be convergence towards a lower constant value around 500 cm^{-1}, quite different from the previous calculations [16, 17] which predicted an increase in that wavenumber with chain length. Throughout, the absolute intensities of the *cis*-bending vibrations are relatively small, with the largest value of 12.6 km mol^{-1} calculated for ω_{21}. The bending vibration of lowest wavenumber (ω_{27}) is predicted at 17.4 cm^{-1}. This value is expected to provide a good approximation to the corresponding anharmonic wavenumber.

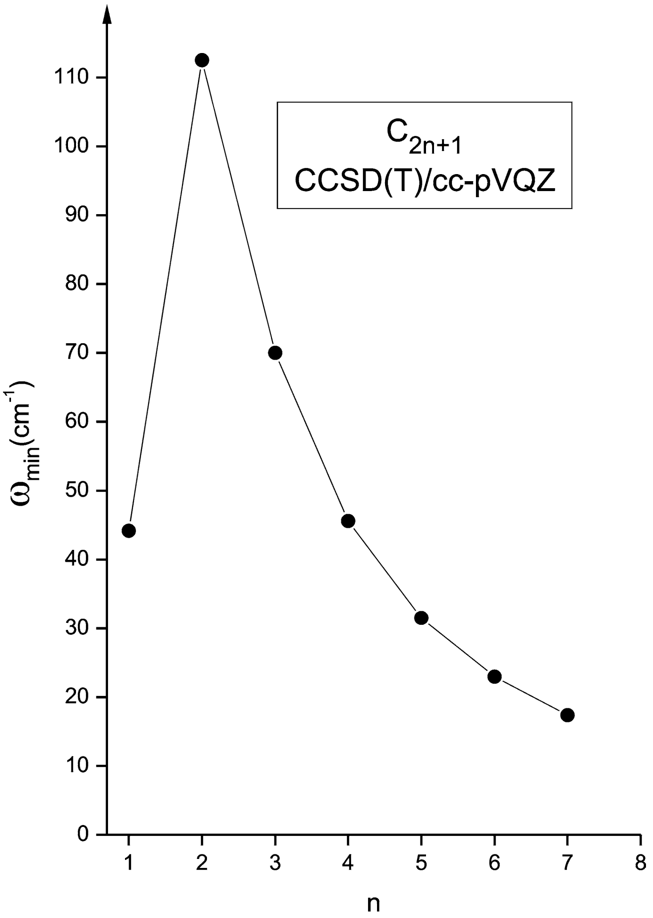

Fig. 4 CCSD(T)/cc-pVQZ wavenumbers of the lowest bending vibration of C_{2n+1} species

3 Conclusions

On the basis of CCSD(T) calculations with the cc-pVQZ basis set and employing an empirical correction established earlier ([22] and references therein), accurate equilibrium structures have been obtained for linear C_{13} and C_{15}. The ground-state rotational constant of the latter is estimated to be 92.2(1) MHz. This value should be of help to experimentalists in the analysis of forthcoming high-resolution spectroscopic investigations of this species. The IR active bending vibrations (π_u symmetry) of C_{13} and C_{15} have been studied within the harmonic approximation which appears to work well for the fairly normal semi-rigid molecules. The cis-bending vibrations with highest wavenumber are predicted close to 500 cm^{-1}, ca. 300 cm^{-1} below the results of previous SCF, CASSCF and B3LYP calculations with the cc-pVDZ basis for linear C_{13} [16, 17].

Figure 4 displays CCSD(T)/cc-pVQZ values for the lowest harmonic wavenumber of carbon chains of type C_{2n+1}. Again, C_3 provides the drastic exception while the results for the longer carbon chains show rather smooth behavior.

Throughout, calculated IR intensities for the *cis*-bending vibrations of linear C_{13} and C_{15} are smaller than 15 km mol^{-1}. For comparison, analogous calculations yield a large value of

2494 km mol^{-1} for the ν_3 band of C_5 which has been observed in IRC+10216. On the basis of the present theoretical study, the chances to observe C_{13} or C_{15} through IR active bending vibrational transitions are considered to be poor.

Acknowledgements The author gratefully acknowledges friendship and collegiality with Prof. Hermann Stoll over a period of more than 30 years and wishes him the very best for the future. He thanks Profs. H.-J. Werner (University of Stuttgart) and P. J. Knowles (University of Cardiff) for continuously providing him with the latest version of MOLPRO. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged. The author wishes to thank Dr. R. Oswald for his help with the solution of a number of hardware and software problems in the course of the present work.

References

1. Weltner W Jr, Van Zee RJ (1989) Chem Rev 89:1713
2. van Orden A, Saykally RJ (1998) Chem Rev 98:2313
3. Mladenović M, Schmatz S, Botschwina P (1994) J Chem Phys 101:5891 and references therein
4. Hinkle KH, Keady JJ, Bernath PF (1988) Science 241:1319
5. Cernicharo J, Goicoechea JR, Caux E (2000) Astrophys 534:L199
6. Giesen TF, van Orden AO, Cruzan JD, Provencal RA, Saykally RJ, Gendriesch R, Lewen F, Winnewisser G (2001) Astrophys J 551:L181; erratum (2001) ibid 555:L77
7. Huggins W Proc R Soc London, 1881, 33:1; 1882, 34:148
8. Jørgensen UG (1994) In: Jørgensen UG (ed.) Molecules in the stellar environment. Springer, Berlin Heidelberg New York
9. Maier JP, Lakin NM, Walker GAH, Bohlender DA (2001) Astrophys J 553:267
10. Oka T, Thorburn JA, McCall BJ, Friedman S, Hobbs LM, Sonnentrucker P, Welty DE, York DG (2003) Astrophys J 582:823
11. Cernicharo J, Goicoechea JR, Benilan Y (2003) Astrophys J 580:L157
12. Bernath PF, Hinkle KH, Keady JJ (1989) Science 244:562
13. Giesen TF, van Orden A, Hwang HJ, Fellers RS, Provencal RA, Saykally RJ (1994) Science 265:756
14. Neubauer-Guenther P, Giesen TF, Berndt U, Fuch G, Winnewisser G (2002) Spectrochim Acta A 59:431
15. Bleil R, Tao F-M, Kais S (1994) Chem Phys Lett 229:491
16. Martin JML, Taylor PR (1995) Chem Phys Lett 240:521
17. Martin JML, El-Yazal J, Francois J-P (1996) Chem Phys Lett 252:9
18. Dunning TH Jr (1989) J Chem Phys 90:1007
19. Botschwina P (2000) Theor Chem Acc 104:160
20. Botschwina P (2002) Chem Phys Lett 354:148
21. Botschwina P (2003) Phys Chem Chem Phys (Invited Article) 5:3337
22. Botschwina P (2005) Mol Phys 103:1441
23. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) Chem Phys Lett 157:479
24. Werner H-J, Knowles PJ (2003) with contributions from Amos RD, Bernhardsson A, Berning A, Celani P, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer G, Knowles PJ, Korona T, Lindh R, Lloyd AW, McNicholas SJ, Manby FR, Meyer W, Mura ME, Nicklass A, Palmieri P, Pitzer R, Rauhut G, Schütz M, Schumann U, Stoll H, Stone AJ, Tarroni R, Thorsteinsson T, MOLPRO, version 2002.6, a package of ab initio programs, see http://www.molpro.net
25. Hampel C, Peterson K, Werner H-J (1992) Chem Phys Lett 190:1
26. Deegan MJO, Knowles PJ (1994) Chem Phys Lett 227:321
27. Heath JR, Saykally RJ (1991) J Chem Phys 94:1724
28. Heath JR, Saykally RJ (1993) In: Reynolds JP (ed.) On clusters and clustering, from atoms to fractals. Elsevier Science Publishers BV, Amsterdam
29. Botschwina P (2003) In: Jahrbuch der Akademie der Wissenschaften zu Göttingen, 2002, pp 272–279, Vandenhoeck and Ruprecht, Göttingen
30. Kendall RA, Dunning TH Jr, Harrison RJ (1982) J Chem Phys 96:6796