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Coupled cluster calculations for (potential) interstellar anions: The $C_{2n}H^-$ series ($n = 2–6$)

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ABSTRACT

The coupled cluster variant CCSD(T) in conjunction with a large basis set has been used to calculate spectroscopic properties for anions of type $C_{2n}H^-$ ($n = 2–6$), three of which were recently observed in the interstellar medium by means of radio astronomy. Accurate equilibrium structures and electric dipole moments are predicted for all five species. A variety of spectroscopic constants (vibrational wavenumbers, vibration–rotation coupling constants, l-type doubling constants and centrifugal distortion constants) are reported for various isotopomers of C_4H^- and C_6H^-. The harmonic bending vibrations of chains up to $C_{10}H^-$ and HC_9N are analyzed by means of "mass plots" which draw the wavenumbers of interest as a function of the "hydrogen" mass, which is regarded as a continuous variable.

1. Introduction

The presence of molecular anions in interstellar and circumstellar media has been discussed for some time (see, e.g., refs. [1–6]), but only recently four negatively charged molecular ions could be unambiguously identified by radio astronomy, following their previous detection by means of microwave (MW) spectroscopy at Harvard. The small list comprises the three members of the $C_{2n}H^-$ series with $n = 2–4$ and the anion C_3N^-. The latter was dealt within four recent papers [7–10]; here we will concentrate on the carbon chains of type $C_{2n}H^-$. In 2006, McCarthy et al. [11] succeeded to measure 17 lines of the pure rotational spectrum of C_6H^- by means of Fourier-transform MW spectroscopy and determined precise values for the ground-state rotational constant B_0 and the corresponding quartic centrifugal distortion constant, termed here D_0^J. With the laboratory data at hand, C_6H^- could be readily identified as the carrier of a series of radio lines with rotational constant 1377 MHz, which were first observed by Kawaguchi et al. in the circumstellar envelope of the evolved carbon star IRC + 10216 [12]. In July 2006, the rotational lines $J = 4–3$ and $5–4$ were also observed in the dense molecular cloud TMC-1 by means of the 100 m Green Bank Telescope [11]. In the meantime, C_6H^- was further detected toward the low-mass star-forming region L1527 [13].

The astronomical detection of C_4H^-, the second interstellar anion, was reported by Cernicharo et al. [14], following laboratory work at the Harvard-Smithsonian Center for Astrophysics [15]. In the latter paper, nine rotational transitions were also reported for C_8H^- which was subsequently found in both TMC-1 [16] and IRC + 10216 [17,18]. A positive detection of C_4H^- was recently made toward protostar L1527 [19,20].

Despite the noted great success of MW spectroscopy and radio astronomy, the present knowledge of spectroscopic properties for free $C_{2n}H^-$ ions with $n > 1$ is still limited. In 1998, Taylor et al. [21] published photoelectron (PE) spectra for C_4H^-, C_6H^-, and C_8H^-. Anion PE spectroscopy traditionally delivers only little spectroscopic information on the anions, but may yield a wealth of spectroscopic data for the corresponding neutrals. Quite recently, results of higher resolution slow electron velocity-map imaging (SEVI) spectroscopy of the C_4H^- and C_4D^- anions were reported [22]. Some weak peaks were observed, which were proposed to "originate from a vibrationally excited anion state with frequencies of around 330 cm^{-1} in C_4H^- and 310 cm^{-1} in C_4D^-."

Electronic absorption spectra of $C_{2n}H^-$ species with $n = 4–7$, mass-selected and codeposited with excess neon at 6 K, were published by Grutter et al. [23]. These authors were also able to observe mid-infrared bands for the four anions considered. Since only one

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or a maximum of two bands was found per species, no assignment of the underlying vibrations could be given. In a second paper [24], the spectroscopic work was extended to longer chains ($n = 8$–12) and, making use of the techniques of resonant two-colour electron photodetachment, the first gas-phase electronic absorption spectra of the anions with $n = 5$–10 could be recorded. More recently, the electronic spectra of $C_{2n}H^-$ and $C_{2n}D^-$ ions with $n = 2$–4 were observed in the gas-phase using photodetachment spectroscopy [25]. The first gas-phase electronic spectra with rotational structure for C_4H^- and C_4D^- were observed by Pachkov et al. [26].

Anions of type $C_{2n}H^-$ with $n > 1$ have also been the subject of a number of quantum-chemical studies. C_4H^- and C_6H^- were investigated by Natterer and Koch [27], who attempted to establish accurate values for the adiabatic electron affinities of the corresponding radicals and for the CH bond dissociation energies and the gas-phase acidities of the polyynes HC_4H and HC_6H. Earlier work at Göttingen [28] was devoted to a study of C_4H^- by means of coupled cluster theory, making use of the popular variant CCSD(T) [29] and a basis set of 169 contracted Gaussian-type orbitals (cGTOs). Major emphasis was laid on the prediction of wavenumbers and absolute infrared intensities for a variety of stretching vibrational transitions up to higher overtones, and the second highest band (ν_2) with origin predicted at 2093 cm^{-1} was found to be by far the most intense vibration. In a systematic application of six different density functional methods to various molecules, Brown et al. [30] studied linear C_6H^- and reported equilibrium structures and harmonic vibrational frequencies. Results of calculations with the popular hybrid density functional B3LYP and the small 6–31G* basis set were reported by Allamandola et al. [31], who concentrated on predictions for the astronomical interesting mid-infrared vibrational transitions for chains up to $C_{12}H^-$. Ab initio calculations at the Hartree–Fock (HF) and configuration interaction singles (CIS) level were published by Kirkwood et al. for linear $C_{10}H^-$ and $C_{12}H^-$ [24]. These authors quoted equilibrium bond lengths and scaled harmonic vibrational wavenumbers for both the electronic ground states and excited $^1\sum^+$ states of both anions. In 2000, results of CCSD(T) calculations were published for C_6H^- by Aoki [32], who reported a scaled ground-state rotational constant of 1377 MHz. The theoretical study of Blanksby et al. [5], mostly carried out by B3LYP and using moderately large basis sets, considered chains up to $C_{10}H^-$ and reported electron affinities for the neutrals and electric dipole moments for the anions. Results of B3LYP calculations were also published by Pan et al. [33] for C_mH^- ions up to $m = 10$ in conjunction with mass spectrometric measurements of the abundance of the anions, which were produced by gas-feed Cs sputtering from different chrystallographic forms of a carbon display. The microwave spectroscopic investigations discussed above [11,15] were accompanied by equilibrium structure determinations at the CCSD(T) level with the medium-sized cc-pVTZ basis set [34] and the calculation of equilibrium quartic centrifugal distortion constants (termed D_e^J) and vibrational contributions to the ground-state rotational constants. Finally, in the course of the present work, we were informed of a recent theoretical study by Herbst and Osamura [35], who made use of B3LYP calculations with the aug-cc-pVTZ basis set [34,36] in order to calculate rate coefficients for the radiative attachment reactions between the radicals C_mH ($m = 2$–8) and electrons, thereby considering two electronic states of the anions in each case.

The present paper is devoted to a rather extensive theoretical investigation of the electronic ground-states of the five closed-shell anions $C_{2n}H^-$ ($n = 2$–6) at a uniform high level of calculation (CCSD(T) with a large basis set). Particular emphasis will be given to the prediction of accurate equilibrium structures and electric dipole moments, as well as to a thorough investigation of the bending vibrations in comparison with results for the isoelectronic cyanopolyynes ($HC_{2n-1}N$). Various further spectroscopic properties such as vibration–rotation coupling constants, l-type doubling constants and centrifugal distortion constants are calculated as well. Throughout, isotope effects are studied in considerable detail.

2. Details of calculations

The present theoretical study of the anions $C_{2n}H^-$ ($n = 2$–6) mostly makes use of the well-known coupled cluster variant CCSD(T) [29], employing the MOLPRO package of ab initio programs [37–39]. A uniform basis set was used in the electronic structure calculations which consists of Dunning's correlation consistent polarized valence quadruple-zeta (cc-pVQZ) basis [33] for all atoms. The terminal carbon atoms, which carry most of the negative charge of the anions, are described by additional 25 cGTOs from the augmented set [35]. For brevity, the complete basis set employed is denoted as "vqz+". The largest calculations carried out (for $C_{12}H^-$) comprise 715 cGTOs. In calculations for the neutral polyynes $HC_{2n}H$, the original cc-pVQZ basis (briefly: vqz) was employed. Throughout, valence electrons were correlated in the coupled cluster calculations.

Besides the spectroscopic constants which determine the position of radioastronomical lines (here: B_0 and D_0^J), electric dipole moments are important quantities as they govern the intensities of pure rotational transitions. In the present work, five different methods are employed in a theoretical investigation of the equilibrium dipole moments (μ_e): Hartree–Fock Self-Consistent Field (HF-SCF), second-order perturbation theory according to Møller and Plesset (MP2) and its spin-component scaled variant (SCS-MP2) as introduced by Grimme [40], coupled cluster with single and double excitation operators (CCSD) and finally CCSD(T), which includes connected triple substitutions in a perturbative way. Within the post-Hartree–Fock calculations, the correlation contributions to the electric dipole moments are calculated as numerical first derivatives of the correlation energies with respect to the strength of a homogenous electric field of ±0.0001 atomic units. These were then added to the corresponding HF-SCF values, obtained as expectation values, to yield the total dipole moments.

For the anions up to $C_{10}H^-$, near equilibrium potential energy functions (PEFs) and electric dipole moments functions (EDMFs) have been calculated pointwise by CCSD(T)/vqz+. Using very small distortions out of equilibrium and tight thresholds in the electronic structure calculations, complete cubic force fields have been calculated numerically for the smaller chains C_4H^- and C_6H^-. In conjunction with the equilibrium structures and the nuclidic masses, conventional second-order perturbation theory in normal coordinate space was then used to calculate a variety of spectroscopic constants. These include harmonic vibrational wavenumbers ω_r, vibration–rotation coupling constants α_r, l-type doubling constant q_t^e and q_e^J and quartic centrifugal distortion constants D_e^J. From the vibration–rotation coupling constants, the vibrational contribution to the ground-state rotational constant B_e may be approximately calculated according to the formula

$$\Delta B_0 = B_e - B_0 \approx \frac{1}{2}\sum_r \alpha_r d_r \tag{1}$$

In Eq. (1), d_r is a degeneracy factor (1 for stretching vibrations and 2 for bending vibrations).

Anharmonicity effects on vibrational wavenumbers and IR intensities of the stretching vibrations have been considered for C_4H^-, C_6H^-, and the corresponding deuterated species. We made use of a well-established stretch-only model which neglects the relatively small anharmonic interaction with the bending modes [41]. From the vibrational wavefunctions and EDMFs, absolute IR absorp-

Table 1
CCSD(T) equilibrium bond lengths for linear molecules of type $C_{2n}H^-$ and $HC_{2n}H$ ($n = 1$–6)[a]

Distance[b]	C_2H^-	C_4H^-	C_6H^-	C_8H^-	$C_{10}H^-$	$C_{12}H^-$[c]
CC1	1.25006 (1.20648)	1.25681 (1.21191)	1.26094 (1.21339)	1.26338 (1.21380)	1.26497 (1.21400)	1.2662 (1.2141)
CC2		1.37275 (1.37686)	1.35660 (1.37024)	1.34876 (1.36849)	1.34407 (1.36781)	1.3409 (1.3675)
CC3		1.22509 (1.21191)	1.23425 (1.21872)	1.23896 (1.22079)	1.24151 (1.22153)	1.2434 (1.2218)
CC4			1.36286 (1.37024)	1.34834 (1.36237)	1.34122 (1.36009)	1.3371 (1.3592)
CC5			1.22186 (1.21339)	1.23143 (1.22079)	1.23647 (1.22319)	1.2388 (1.2240)
CC6				1.36401 (1.36849)	1.35081 (1.36009)	1.3444 (1.3577)
CC7				1.21957 (1.21380)	1.22910 (1.22153)	1.2333 (1.2240)
CC8					1.36515 (1.36781)	1.3530 (1.3592)
CC9					1.21792 (1.21400)	1.2269 (1.2218)
CC10						1.3662 (1.3675)
CC11						1.2169 (1.2141)
CH	1.07089 (1.06336)	1.06108 (1.06332)	1.06137 (1.06355)	1.06181 (1.06366)	1.06217 (1.06375)	1.0625 (1.0638)

[a] Basis sets: vqz+ for anions and vqz for neutral molecules (in parentheses). Throughout, valence electrons are correlated.

[b] CC distances are numbered from left to right according to the chemical formula.

[c] Lower numerical accuracy (ca. 10^{-4} Å) compared to smaller chains.

tion intensities for transitions from the vibrational ground-state $|0\rangle$ to final state $|f\rangle$ were approximately calculated by the well-known formula (see, e.g., ref. [42]):

$$A_{f0} = \frac{\pi N_A}{3\hbar c_0 \varepsilon_0} \tilde{\nu}_{f0} |\underline{\mu}_{f0}|^2 \qquad (2)$$

In Eq. (2), N_A is Avogadro's constant, $\hbar$ Planck's constant divided by 2π, c_0 the vacuum velocity of light, ε_0 the permittivity of vacuum, $\tilde{\nu}_{f0}$ the vibrational wavenumber and $\underline{\mu}_{f0}$ is the corresponding vibrational transition moment.

3. Results and discussion

3.1. Equilibrium structures and electric dipole moments

CCSD(T) equilibrium structures for the linear anions $C_{2n}H^-$ and the corresponding polyynes $HC_{2n}H$ are listed in Table 1. Since only valence electrons were correlated, the calculations lack core–valence and core–core correlation; there are additional minor errors resulting from the use of incomplete basis sets and the neglect of higher substitutions (in particular, connected quadruples) in the chosen coupled cluster variant. As has been investigated earlier for the isoelectronic series of dicyanopolyynes $NC_{2n-2}N$ [43], valence-only CCSD(T) calculations with basis sets of vqz quality overestimate the short bond lengths of conjugated triple-bonded systems by 0.003 Å, while the longer ones are too long by 0.005 Å.

Owing to only slight changes in electron correlation effects, the differences in equilibrium bond lengths between anions and the corresponding neutral polyynes are expected to be reproduced very well, with expected errors of just a few ten-thousands of an Ångstrøm unit. Upon heterolytic CH bond fission in a given polyyne, the adjacent CC bond experiences the largest change; the calculated differences range from 0.0436 Å (C_2H^-) up to 0.0521 Å ($C_{12}H^-$). The CCSD(T)/vqz+ equilibrium bond length of the terminal CC bond in $C_{12}H^-$ of 1.26616 thus already comes close to the range of equilibrium bond lengths for heterocumulenic carbon chains. For example, the shortest carbon–carbon bond of isoelectronic $C_{11}O$, as calculated by CCSD(T)/vqz, is 1.26999 Å [44].

Estimates of accurate equilibrium structures for the linear anions $C_{2n}H^-$ ($n = 2$–6) are made along the lines described in earlier papers of the corresponding author (see, e.g., ref. [43]). Here, we make use of correction parameters which are taken over from HC_5N (isoelectronic with C_6H^-), for which an accurate mixed experimental/theoretical equilibrium structure has been determined earlier [45]. Specifically, the shorter and longer CCSD(T)/vqz+ carbon–carbon equilibrium bond lengths are reduced by 0.0030 and 0.0048 Å, respectively, with the exception of the terminal carbon bond which occupies an intermediate position (see above). The latter is reduced by 0.0034 Å, a value obtained through adjustment to an accurate equilibrium rotational constant (B_e) for C_6H^- (see Section 3.2). For the remaining CH distance we use a correction of −0.0020 Å, again taken over from HC_5N (see also Fig. 1 of ref. [43]). The recommended equilibrium structures obtained in the described way are shown in Fig. 1. The individual equilibrium bond lengths are expected to be accurate to ca. 0.0005 Å. Equilibrium rotational constants for the longer chains C_8H^-, $C_{10}H^-$, and $C_{12}H^-$, as calculated from the recommended equilibrium structures are 582.6, 299.4, and 173.8 MHz, respectively. The present B_e value for C_8H^- is smaller than the experimental B_0 value [15] by only 0.7 MHz. We therefore expect that the B_e predictions for the two longer chains will also provide good estimates for the corresponding ground-state rotational constants and may thus be of help to experimentalists in the search for rotational spectra of the longer chains.

Electric dipole moments were calculated at the recommended equilibrium structures and are listed in Table 2. Values for five different methods are quoted, those obtained by CCSD(T) are expected to be the most reliable ones. As has been noted earlier [5,15], the dipole moments increase strongly with increasing chain length. According to the present calculations, they reach almost 20 D for $C_{12}H^-$. The differences between CCSD(T) and Hartree–Fock values do not exceed 0.25 D. At the CCSD level, the correlation contributions are strongly overestimated and are largely cancelled by the contributions from the connected triple substitutions. In comparison with CCSD(T), conventional MP2 does a quite good job, while SCS-MP2 shows differences of up to 0.50 D.

3.2. Complete cubic force fields and derived spectroscopic constants for different isotopomers of C_4H^- and C_6H^-

Complete cubic force fields for C_4H^- and C_6H^- were calculated by CCSD(T) with the vqz+ basis set. Spectroscopic constants calculated therefrom are listed in Table 2 (six isotopomers of C_4H^-) and

Table 2
Equilibrium electric dipole moments (in D) for $C_{2n}H^-$ ions[a]

n	HF-SCF	MP2	SCS-MP2	CCSD	CCSD(T)
2	6.044	6.283	6.542	6.391	6.335
3	8.837	9.166	9.286	9.266	8.999
4	12.197	12.462	12.737	12.851	12.367
5	15.717	15.649	16.144	16.505	15.707
6	19.530	19.028	19.782	20.443	19.284

[a] Dipole moments were calculated at the recommended equilibrium structures (see Fig. 1) and refer to the molecular center-of-mass coordinate system.

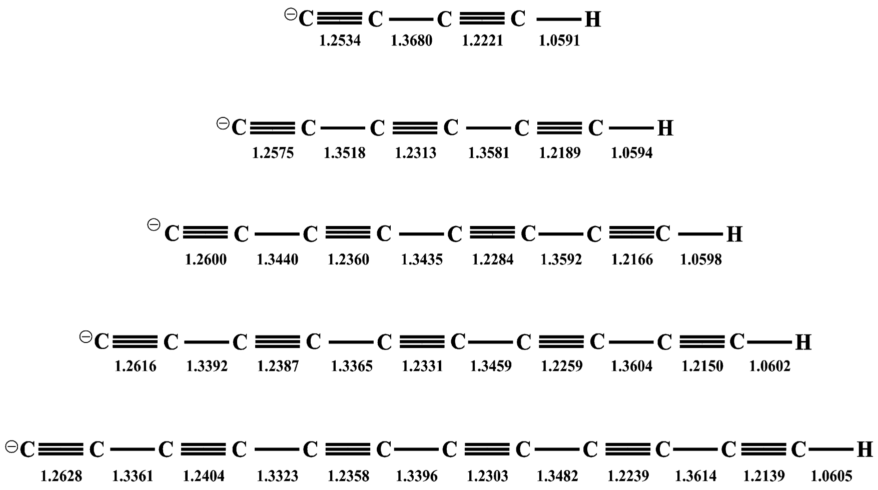

Fig. 1. Recommended equilibrium structures for $C_{2n}H^-$ anions (bond lengths in Å).

Table 3
CCSD(T)/vqz+ spectroscopic constants for C_4H^- isotopomers[a]

	C_4H^-	13(1)	13(2)	13(3)	13(4)	C_4D^-
ω_1	3467.6	3467.6	3467.6	3466.9	3451.8	2656.3
ω_2	2122.7	2117.8	2105.9	2084.9	2109.7	2068.6
ω_3	1927.6	1904.9	1895.4	1915.5	1915.4	1875.5
ω_4	879.8	866.0	875.3	875.0	868.5	865.6
ω_5	510.6	510.3	504.7	501.4	510.3	493.9
ω_6	397.4	397.4	397.2	395.5	393.8	316.5
ω_7	216.2	213.7	212.9	215.1	215.2	208.2
α_1	7.036	6.670	7.012	6.918	6.449	10.713
α_2	23.293	22.144	21.953	23.270	23.254	21.382
α_3	15.638	15.595	15.849	14.707	14.706	12.159
α_4	10.763	10.122	10.782	10.800	10.195	9.424
α_5	−7.146	−6.883	−6.917	−6.866	−6.917	−7.250
α_6	−6.477	−6.168	−6.514	−6.529	−5.825	−8.816
α_7	−15.000	−14.585	−14.485	−14.789	−14.487	−13.132
ΔB_0	−0.258	−0.371	−0.118	−0.336	0.073	−2.358
q_5^e	3.689	3.442	3.693	3.719	3.472	3.287
q_6^e	3.826	3.565	3.793	3.828	3.634	4.131
q_7^e	6.940	6.544	6.979	6.927	6.560	6.207
q_5^J	−1.317	−1.163	−1.294	−1.326	−1.169	−1.301
q_6^J	−3.703	−3.308	−3.683	−3.731	−3.307	−5.117
q_7^J	−17.906	−16.544	−17.732	−17.745	−16.409	−14.558
D_e^J	545	507	542	544	512	451
D_0^J	587.5(1)[b]	547[c]	584[c]	586[c]	552[c]	486[c]

[a] Harmonic vibrational wavenumbers ω_r in cm^{-1}, vibration–rotation coupling constants α_r and l-type doubling constants q_t^e in MHz, quartic equilibrium centrifugal distortion constant D_e^J and q_t^J values in Hz. An obvious shorthand notation is employed to designate ^{13}C monosubstituted isotopomers, e.g., 13(1) stands for $^{13}CCCCH^-$.

[b] Experimental ground-state value [15].

[c] Obtained by scaling the D_e^J values (see the text).

Table 3 (eight isotopomers of C_6H^-). According to vast experience with CCSD(T) calculations employing basis sets of cc-pVQZ quality, the harmonic stretching vibrational wavenumbers are expected to have errors of less than 10 cm^{-1}, while those for the bending vibrations should not exceed 5 cm^{-1}. High accuracy is also expected for the vibration–rotation and l-type doubling constants. Differences from precise experimental values of just a few percent were observed for various isotopomers of the isoelectronic molecules HC_3N and HC_5N [43,46,47].

Some comparison with experiment is possible for the bending vibrations of C_4H^-, C_6H^-, and their deuterated species. We predict harmonic bending vibrational wavenumbers (in cm^{-1}) of $\omega_5 = 511$ (494), $\omega_6 = 397$ (317), and $\omega_7 = 216$ (208) for C_4H^- and C_4D^- (in parentheses). The lowest bending vibration of each isotopomer is expected to exhibit only very small effects of vibrational anharmonicity (see also Section 3.5). The present harmonic values are within the error bars of the experimental results published by Pino et al. [25]. Anharmonicity effects are probably more important for the ν_6 vibrations which involve significant CCH(D) bending character. For C_4H^- (C_4D^-), approximate experimental values are 430 (396) cm^{-1} [29] and 330 (310) cm^{-1} [22].

The present calculations for C_6H^- support the assignment made by Pino et al. [25], who assigned the peak off from the adiabatic (0_0^0) transition by −860 cm^{-1} to the transition 9_2^0. This means that the bending vibrational wavenumber ν_9 of C_6H^- should have a value of ca. 430 cm^{-1}, of which compares well with the calculated harmonic wavenumber of 440 cm^{-1}. The lowest harmonic bending vibration (ω_{11}) of C_6H^- and C_6D^- is calculated at 102.4 and 99.0 cm^{-1}, respectively, rather close to the corresponding values for HC_5N and DC_5N (see Section 3.5). The CCSD(T) harmonic bending vibrational wavenumbers ω_{10} for C_6H^- and C_6D^- are 237.8 and 234.5 cm^{-1}, respectively. Therefore, we may rule out the transition

Table 4
CCSD(T)/vqz+ spectroscopic constants for C_6H^- isotopomers[a]

	C_6H^-	13(1)	13(2)	13(3)	13(4)	13(5)	13(6)	C_6D^-
ω_1	3468.3	3468.3	3468.3	3468.3	3468.3	3467.5	3452.3	2660.9
ω_2	2185.1	2184.9	2183.3	2160.5	2150.0	2176.0	2183.0	2177.9
ω_3	2100.0	2095.9	2087.8	2084.8	2099.4	2066.2	2084.5	2033.1
ω_4	1936.1	1915.2	1900.7	1933.8	1927.4	1928.1	1929.8	1903.2
ω_5	1169.9	1160.9	1169.4	1154.6	1155.9	1169.0	1162.9	1159.3
ω_6	621.6	613.8	616.8	621.4	621.4	616.8	614.8	613.9
ω_7	506.4	506.3	504.8	502.5	502.2	505.1	506.1	496.5
ω_8	481.6	481.4	477.9	474.5	481.6	481.0	481.1	447.8
ω_9	440.1	440.1	439.6	439.8	438.1	430.8	436.3	369.1
ω_{10}	237.8	236.1	234.2	236.9	235.9	237.1	237.5	234.5
ω_{11}	102.4	101.3	102.4	101.8	101.2	102.4	101.6	99.0
α_1	0.980	0.937	0.966	0.980	0.976	0.949	0.911	1.595
α_2	5.075	4.902	4.966	4.679	4.848	5.164	5.015	4.905
α_3	3.397	3.261	3.249	3.686	3.506	3.246	3.370	3.244
α_4	2.801	2.848	2.784	2.776	2.794	2.621	2.646	2.252
α_5	3.026	2.895	3.013	2.983	2.988	3.020	2.908	2.780
α_6	1.171	1.117	1.158	1.167	1.168	1.159	1.120	1.084
α_7	−1.332	−1.287	−1.244	−1.147	−1.267	−1.334	−1.297	−1.632
α_8	−1.229	−1.200	−1.283	−1.367	−1.248	−1.175	−1.165	−1.442
α_9	−1.435	−1.381	−1.417	−1.436	−1.427	−1.423	−1.384	−1.149
α_{10}	−2.629	−2.586	−2.533	−2.618	−2.608	−2.584	−2.545	−2.411
α_{11}	−2.984	−2.888	−2.936	−2.951	−2.933	−2.947	−2.903	−2.799
ΔB_0	−1.384	−1.363	−1.346	−1.383	−1.343	−1.383	−1.308	−1.505
q_7^e	0.309	0.293	0.302	0.305	0.309	0.304	0.295	0.296
q_8^e	0.316	0.298	0.313	0.324	0.316	0.307	0.301	0.321
q_9^e	0.335	0.317	0.330	0.336	0.338	0.340	0.319	0.336
q_{10}^e	0.559	0.532	0.555	0.559	0.562	0.550	0.531	0.517
q_{11}^e	1.252	1.195	1.225	1.256	1.265	1.228	1.198	1.178
q_7^J	0.002	0.004	0.003	−0.000	0.005	0.003	0.002	−0.021
q_8^J	−0.045	−0.042	−0.045	−0.046	−0.051	−0.049	−0.039	−0.031
q_9^J	−0.051	−0.046	−0.048	−0.050	−0.049	−0.047	−0.049	−0.054
q_{10}^J	−0.225	−0.212	−0.220	−0.226	−0.227	−0.219	−0.208	−0.194
q_{11}^J	−1.264	−1.180	−1.218	−1.262	−1.271	−1.225	−1.186	−1.153
D_e^J	28.9	27.2	28.4	28.8	28.8	28.5	27.3	25.7
D_0^J	32.35(1)[b]	30.4[c]	31.8[c]	32.2[c]	32.2[c]	31.9[c]	30.5[c]	28.8[c]

[a] See footnote ‘a’ of Table 3.
[b] Experimental ground-state value [11].
[c] Obtained by scaling the D_e^J values (see the text).

10^0_2 as being responsibly for the peaks with $\Delta\nu$ values of −244 (C_6H^-) and −214 (C_6D^-) cm^{-1} (see Table 2 of ref. [25]), while the alternative assignment 11^0_2 may be valid.

The calculated ΔB_0 values of Tables 3 and 4 may be combined with the experimental B_0 values [11,15] to produce rather accurate B_e values. These are B_e (C_4H^-) = 4654.7 MHz, B_e (C_6H^-) = 1375.5 MHz, and B_e (C_6D^-) = 1313.0 MHz. As mentioned in Section 3.1, the B_e value for C_6H^- has been employed in the construction of the recommended equilibrium structure for this anion.

Let us now consider the quartic centrifugal distortion constants which are required for an accurate description of the frequencies of rotational transitions. We define the ratio of the experimental value for the ground-state centrifugal distortion constant over the corresponding CCSD(T) equilibrium value by

$$f = \frac{D_0^J(\text{exp.})}{D_e^J(\text{theor.})} \quad (3)$$

With the data given in Table 3, the f value for C_4H^- is obtained to be 1.078, very close to the corresponding value of 1.075 for isoelectronic HC_3N (see ref. [48] and references therein). An almost identical value applies for DC_3N. It seems therefore to be justified well

Table 5
Wavenumbers (in cm^{-1}) and absolute IR intensities (in km mol^{-1}, in parentheses) for stretching fundamentals of C_4H^-, C_6H^-, and their deuterated species[a]

Band	C_4H^-	C_4D^-	C_6H^-	C_6D^-
ν_1	3357 (67)	2597 (166)	3359 (112)	2600 (187)
ν_2	2098 (526)	2042 (418)	2154 (1476)	2146 (1397)
ν_3	1905 (4)	1853 (5)	2077 (46)	2009 (43)
ν_4	871 (13)	857 (13)	1913 (290)	1880 (249)
ν_5			1159 (21)	1148 (22)
ν_6			617 (27)	609 (27)

[a] CCSD(T)/vqz+. Results from variational calculations with a stretch-only vibrational Hamiltonian.

Table 6
Harmonic stretching vibrational wavenumbers (in cm^{-1}) and absolute IR intensities (in km mol^{-1}; in parentheses) for C_8H^-, $C_{10}H^-$, and their deuterated species[a]

Band	C_8H^-	C_8D^-	$C_{10}H^-$	$C_{10}D^-$
ω_1	3466.2 (153)	2663.2 (221)	3464.1 (180)	2664.8 (215)
ω_2	2201.5 (190)	2188.5 (408)	2224.2 (3)	2217.6 (8)
ω_3	2159.9[b] (2793)	2153.1 (3014)	2175.5 (237)	2162.0 (693)
ω_4	2065.0[b] (1185)	1990.2 (916)	2102.2[c] (6879)	2097.5 (6599)
ω_5	1941.2 (354)	1926.0 (90)	2065.0 (259)	1985.5 (83)
ω_6	1310.7 (0)	1303.8 (0)	1935.8 (1087)	1927.5 (1007)
ω_7	916.7 (42)	908.9 (43)	1388.2 (3)	1383.9 (4)
ω_8	477.7 (35)	473.0 (34)	1090.8 (1)	1084.2 (1)
ω_9			751.9 (56)	746.3 (56)
ω_{10}			386.6 (40)	383.4 (39)

[a] CCSD(T)/vqz+. Valence electrons correlated.
[b] Anharmonic neon matrix values [23]: 2106.5 and 2021.2 cm^{-1} (±1 cm^{-1} accuracy).
[c] Anharmonic neon matrix value [23]: 2039.6 ± 1 cm^{-1}.

Table 7
CCSD(T)/vqz+ harmonic bending vibrational wavenumbers (in cm^{-1}) for C_8H^-, $C_{10}H^-$ and their deuterated species

Band	C_8H^-	C_8D^-	Band	$C_{10}H^-$	$C_{10}D^-$
ω_9	530.0	496.3	ω_{11}	555.9	496.2
ω_{10}	496.3	468.9	ω_{12}	496.2	472.1
ω_{11}	465.1	429.3	ω_{13}	470.7	457.0
ω_{12}	426.7	399.2	ω_{14}	456.9	433.7
ω_{13}	247.5	245.7	ω_{15}	411.7	402.6
ω_{14}	153.6	150.0	ω_{16}	253.5	252.2
ω_{15}	59.7	58.2	ω_{17}	187.0	183.7
			ω_{18}	103.0	101.0
			ω_{19}	39.1	38.3

to use a uniform factor of $f = 1.078$ to scale the calculated D_e^J values of all C_4H^- isotopomers in order to arrive at rather accurate predictions (estimated accuracy: 1%) for the corresponding ground-state values. The latter are quoted in the last line of Table 3. In an analogous way, we arrive at D_0^J predictions for less abundant isotopomers of C_6H^-, as given in the last line of Table 4. In this case, the scaling factor is 1.120, again only slightly larger than the corresponding value for HC_5N, which is $f = 1.110$. The D_0^J value for C_6D^- from the present work is 28.8 Hz, 11% smaller than the experimental value for C_6H^- [11]. The experimental value for C_6D^- from ref. [11], obtained from five rotational transitions observed between 10 and 22 GHz, is as large as 36.04 ± 2.23 Hz, where the quoted error bars correspond to 1σ. We see no reason why the D_0^J value for C_6D^- could be larger than that for C_6H^- and therefore recommend the significantly smaller value established in the present work. It is smaller than the predicted value of 29.5 Hz given in Table 2 of ref. [11] by 2.4%.

Table 8
CCSD(T)/vqz harmonic bending vibrational wavenumbers (in cm^{-1}) for cyanopolyynes[a]

No.	HC_3N	DC_3N	HC_5N	DC_5N	HC_7N	DC_7N	HC_9N	DC_9N
1	670.7	523.1	650.5	508.6	642.7	502.5	639.5	500.6
2	500.6	498.5	501.0	501.0	498.3	498.2	496.9	496.3
3	223.2	213.1	462.9	458.6	484.1	482.7	489.8	489.7
4			254.0	247.1	435.9	432.2	465.3	463.1
5			106.8	103.3	269.4	264.5	418.1	415.2
6					158.5	154.7	277.6	274.0
7					61.1	59.6	192.6	189.0
8							105.7	103.6
9							39.3	38.6

[a] Experimental gas-phase anharmonic values are: (1) HC_3N: 663.2, 498.5, and 222.4 cm^{-1} [53]. (2) DC_3N: 523.0, 494.5, and 213.0 cm^{-1} [53]. (3) HC_5N: 642.1, 500.9, and 461.1 cm^{-1} [54,55]. (4) DC_5N: 508 and 500 cm^{-1} [55].

3.3. Anharmonic variational calculations for the stretching vibrations of C_4H^- and C_6H^-

The stretching vibrations of linear C_4H^-, C_6H^-, and their deuterated analogues were studied by means of anharmonic variational calculations as briefly described in Section 2. The underlying CCSD(T)/vqz+ potential energy functions represent an extension of the cubic force fields and are based on 201 and 459 energy points for C_4H^- and C_6H^-, respectively. In order to be able to compute absolute IR intensities, electric dipole moment functions were constructed as well. Results for the fundamental stretching vibrations are given in Table 5. The present values for the stretching vibrational wavenumbers of C_4H^- are in close agreement with our previous results [28], differences not exceeding 13 cm^{-1}. The predictions made here for C_4H^-, C_6H^-, and their deuterated species

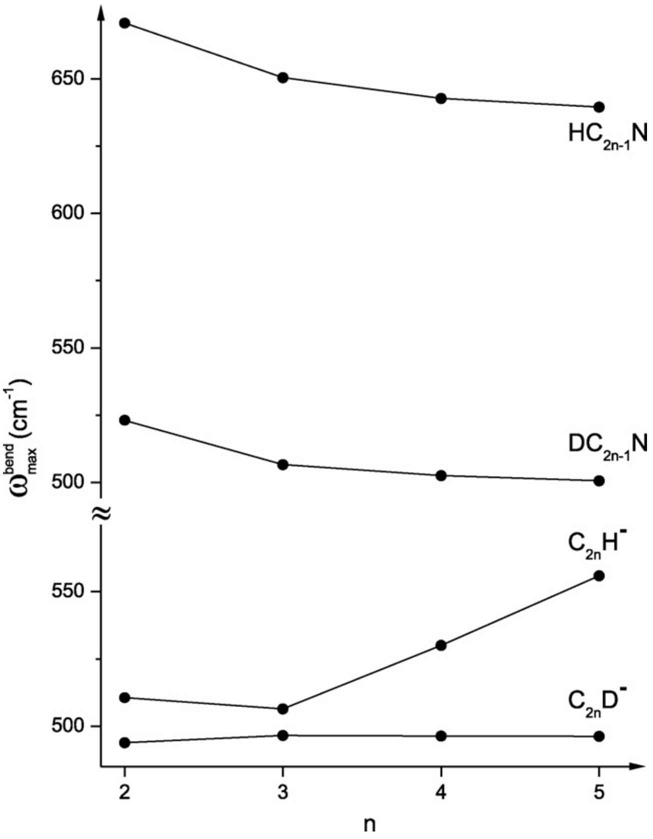

Fig. 2. Comparison of the highest harmonic bending vibrational wavenumbers in the series $C_{2n}H^-$, $HC_{2n-1}N$ and their deuterated analogues.

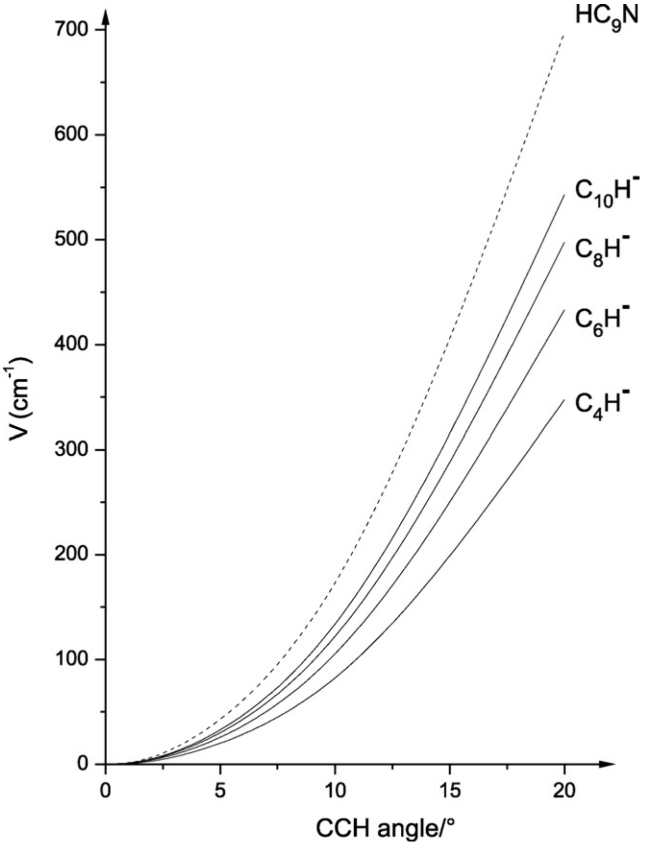

Fig. 3. CCH bending potential functions (CCSD(T)/vqz+) for $C_{2n}H^-$ ($n = 2$–5) and HC_9N.

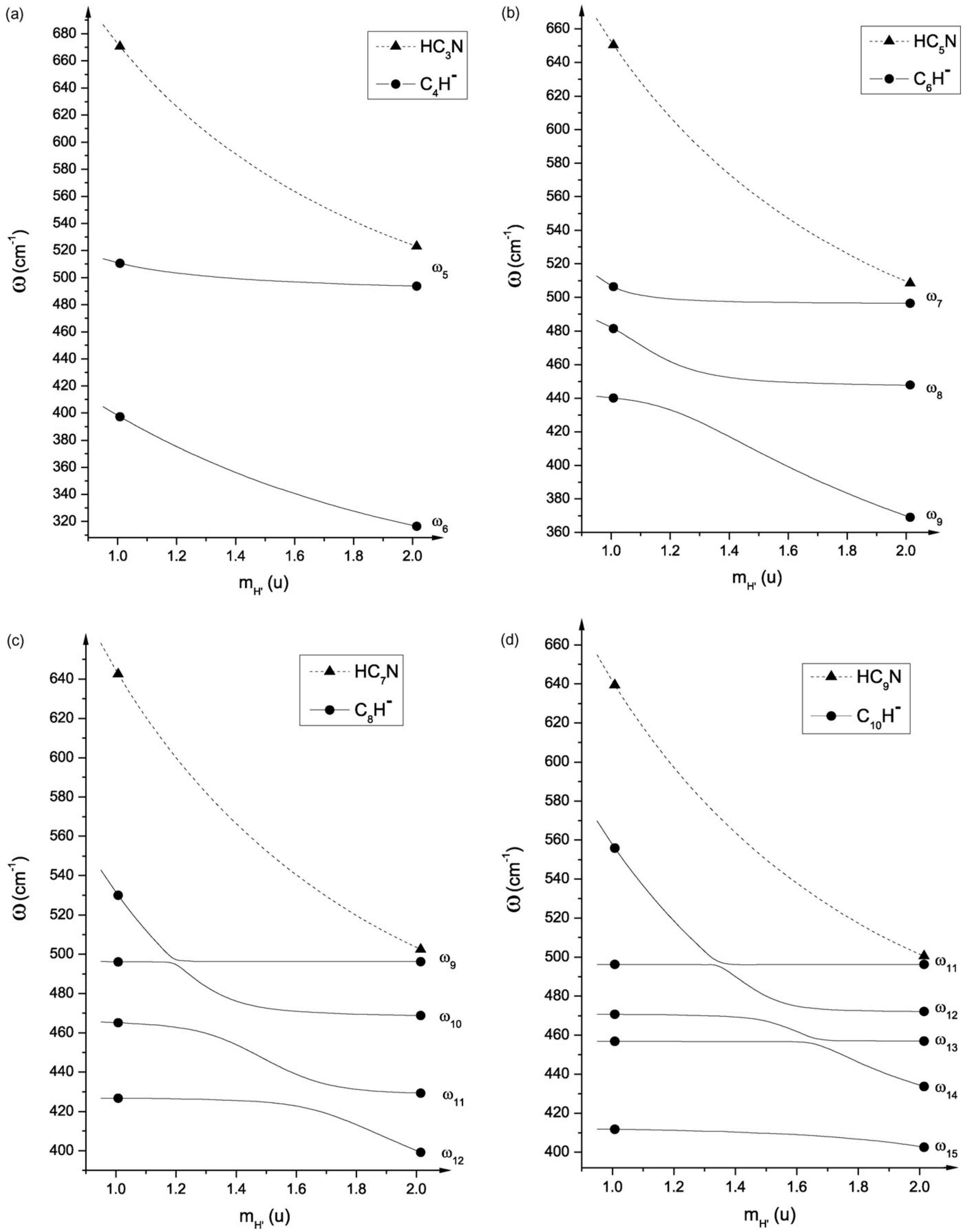

Fig. 4. Variation of highest harmonic bending vibrational wavenumbers with the hydrogen mass $m_{H'}$, taken as a variable, for (a) C_4H^- and HC_3N; (b) C_6H^- and HC_5N; (c) C_8H^- and HC_7N; (d) $C_{10}H^-$ and HC_9N.

should be accurate to ca. 10 cm^{-1} for the heavier-atom stretching vibrations. Neglect of anharmonic stretch-bend interaction is probably more important for the CH(CD) stretching vibration ν_1 and may well lead to errors in the 20 cm^{-1} range, overestimates being expected. As discussed earlier [28], the IR spectrum of C_4H^- is dominated by a single band, corresponding to the heavier-atom stretching vibration with highest wavenumber (ν_2). The same holds for the longer chain C_6H^-, where the band origin of the ν_2 band is shifted to higher wavenumbers by 56 cm^{-1}, connected with an intensity enhancement of almost a factor of three.

3.4. *Stretching vibrations of C_8H^- and $C_{10}H^-$ within the double-harmonic approximation*

For economical reasons and since we do not expect any unusual anharmonicity effects, the treatment of the stretching vibrations of C_8H^-, $C_{10}H^-$, and their deuterated isotopomers was restricted to the double-harmonic approximation. Results are given in Table 6. For C_8H^-, two strong mid-IR bands (ν_3 and ν_4) are obtained, which is in agreement both with the neon matrix spectra of Grutter et al. [23] and the calculations of Allamandola et al. [31]. Since the errors in the present harmonic wavenumbers and the neon matrix shifts should not exceed a few cm^{-1}, most of the differences between CCSD(T)/vqz+ harmonic and experimental wavenumbers are attributed to vibrational anharmonicity. The ratios ω_i(theor.)/ν_i(exp.) for $i = 3$ and 4 are 1.025 and 1.022, respectively; they appear to be quite reasonable for carbon chains of this size. For comparison, the corresponding ratios for the ν_4 and ν_5 bands of C_7 are 1.031 and 1.018 [49], while those for the ν_5 and ν_6 bands of linear C_9 are 1.036 and 1.028, with experimental values taken from ref. [50].

For the equilibrium centrifugal distortion constant of C_8H^-, we calculate a value of 3.733 Hz, to be compared with an experimental D_0^J value of 4.3(2) Hz. The ratio $f = 1.15$ is in line with the data obtained for C_4H^- and C_6H^- (see Section 3.2). It is also well compatible with $f = 1.142$ as calculated for HC_7N, using experimental data from the paper by Bizzocchi and Degli Esposti [51].

By far the most intense stretching vibration of $C_{10}H^-$ is the ν_4 band, with a calculated harmonic wavenumber of 2102 cm^{-1} and an anharmonic experimental counterpart of 2040 cm^{-1} [23]. The ratio of wavenumbers is 1.030 which is an indication that the anharmonicity contribution to the wavenumber of the most intense stretching vibration becomes larger with increasing chain length. A similar situation is found for the pure carbon chains of type C_{2n+1} (see Fig. 5 of ref. [52]). According to the present calculations, the other mid-IR stretching vibrations of $C_{10}H^-$ have intensities smaller by at least a factor of six with respect to ν_4 and may thus have escaped experimental detection. Again, agreement with the previous theoretical work by Allamandola et al. [31] is quite good.

3.5. *Harmonic bending vibrational wavenumbers: comparison of $C_{2n}H^-$ and $HC_{2n-1}N$ ($n = 2$–5)*

CCSD(T)/vqz+ harmonic bending vibrational wavenumbers for C_8H^-, $C_{10}H^-$, and the corresponding deuterated anions are listed in Table 7. CCSD(T)/vqz values for the corresponding series of isoelectronic cyanopolyynes $HC_{2n-1}N$ ($n = 2$–5) are given in Table 8. For HC_3N, DC_3N, HC_5N, and DC_5N some comparison with experimental anharmonic values (see footnote to Table 8) is possible, which shows that vibrational anharmonicity plays only a minor role for the fundamental bending vibrations of these species.

In the $C_{2n}H^-$ and $HC_{2n-1}N$ series of molecules, we may roughly divide the harmonic bending vibrations into two classes: one with wavenumbers below 260 cm^{-1} and another with wavenumbers above 395 cm^{-1}. For any vibration of the first class, the difference in wavenumber between the value for an anion and the corresponding cyanopolyyne of the same integer n is rather small, typically less than 5%. For the vibrations with the higher wavenumbers, the situation may be rather different and we will discuss it in some detail, starting with the highest harmonic bending vibration, termed $\omega_{\text{max}}^{\text{bend}}$. The corresponding wavenumbers are graphically displayed in Fig. 2. For the cyanopolyynes $HC_{2n-1}N$, $\omega_{\text{max}}^{\text{bend}}$ is essentially a local HCC bending vibration. The corresponding HCC bending potentials are rather steep and their shape is almost independent of the integer n. Fig. 3 therefore includes only the graph for the longest chain considered, HC_9N. The corresponding curves for the $C_{2n}H^-$ ions are considerably more shallow and strongly increase in steepness with increasing chain length. This change in the CCH bending potentials is mainly responsible for the strong increase in $\omega_{\text{max}}^{\text{bend}}$ when going from $n = 3$ to $n = 5$ (see Fig. 2).

A more detailed insight into the nature of the highest bending vibrations of the two series of molecules as well as their deuterated analogues may be gained by means of so-called “mass plots”, which have been successfully used in the past to describe isotope effects on the proton stretching vibrations of complexes between a rare-gas atom and a linear triatomic cation of type HAB^+ (see ref. [56] and references therein). In the present case, we draw the highest harmonic bending vibrational wavenumbers as a function of the “hydrogen” mass $m_{H'}$, which is taken as a continuous variable. Mass plots for the systems with $n = 2$–5 are shown in Fig. 4a–d. For $n = 2$ (see Fig. 4a), ω_5 of $H'C_3N$ shows a strong variation with $m_{H'}$ and, for HC_3N with $m_{H'} = m_H$, corresponds to an almost local HCC bending vibration. The other bending vibrations (not shown in Fig. 4a) exhibit very little dependence on $m_{H'}$. On the other hand, it is not the highest bending vibration in the C_4H^- system which shows the strongest $m_{H'}$ dependence. Instead, the second highest bending vibration ω_6 is predominantly CCH bending in nature. For the longer chains, the situation is always the same with the cyanopolyynes, but the anions show rather complex behaviour, with avoided crossings occurring between different vibrations (see Fig. 4a–c). In C_6H^-, both ω_7 and ω_8 have significant HCC bending character, whereas $\omega_9(C_6D^-)$ may be safely described as a CCD bending vibration. From C_8H^- on, like in all cyanopolyynes, the highest bending vibration is mostly a local CCH bending vibration, but lower modes carry the major part of CCD bending in the case of the deuterated species.

4. Conclusions

Owing to their recent detection in prominent astronomical sources, anions of type $C_{2n}H^-$ are currently of great interest. Making use of high-level ab initio calculations and taking over corrections from the well-known isoelectronic cyanopolyynes ($HC_{2n-1}N$), accurate equilibrium structures (accuracy in bond lengths: ca. 0.0005 Å) have been established for chains up to $C_{12}H^-$. Quite favourable for microwave spectroscopy and radio astronomy, the electric dipole moments increase strongly with chain length such that a large value of $\mu_e = 19.28$ D is predicted for $C_{12}H^-$. Several spectroscopic data for vibrationally excited states of C_4H^- and C_6H^- are reported which may be of interest to forthcoming MW and radioastronomical studies, keeping in mind that rotational transitions within vibrationally excited states of HC_3N and HC_5N have already been observed in warmer regions of the interstellar medium. Reliable absolute IR intensities are predicted for the stretching vibrations of $C_{2n}H^-$ ions up to $C_{10}H^-$. For the most intense vibrations, good agreement is obtained with the neon matrix isolation IR spectroscopic study of Grutter et al. [23].

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