

Spectroscopic properties of interstellar molecules: Theory and experiment

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Over the past two decades, the identification and characterisation of interstellar molecules has often benefitted from a fruitful interplay between theoretical chemistry, laboratory spectroscopy and (radio) astronomy. The article reports on various examples of this sort, concentrating on carbon chains which represent the most prominent structural motif among currently known interstellar molecules. Results of large-scale coupled cluster calculations are reported for cyanopolyynes (HC_{2n+1}N) up to $n = 5$, the corresponding radicals C_{2n+1}N , linear silicon carbides (SiC_n), carbon–sulfur and pure carbon chains. Throughout, detailed comparison with experimental data is made wherever possible.

1. Introduction

During the past four decades, radio astronomy enabled the detection of an astonishing wealth of molecular species in the interstellar medium (ISM). The current number of known interstellar molecules is around 130 and it is rising at a rate of about four per year.¹ Several non-polar molecules have also been identified in the infrared region of the spectrum. Among these, smaller ones like carbon dioxide or acetylene have been known interstellar molecules for quite some time while the detection of larger molecules such as diacetylene (C_4H_2), triacetylene (C_6H_2) or benzene has been reported only very recently.² The large majority of the unambiguously identified interstellar molecules are carbon chains, with the cyanopolyne HC_{11}N being the longest chain observed so far by radio astronomy. This molecule has actually a remarkable story of “lost and found”. In 1982 and 1985, weak radio lines observed in the circumstellar envelope of the evolved carbon star IRC+10216 and in the cold dust cloud TMC-1, the abbreviation standing for “Taurus Molecular Cloud”, were attributed to HC_{11}N .^{3,4} The assignments were not based on laboratory data as these were not available at that time. Instead, they mainly relied on an extrapolated value of the ground-state rotational constant (B_0) reported by Oka.⁵ For more than ten years, all attempts to confirm the identification by laboratory detection or the observation of further astronomical lines have failed. Finally, in 1996, Thaddeus and coworkers were able to measure 20 rotational transitions of HC_{11}N by means of their newly built Fourier transform (FT) molecular-beam microwave (MW) spectrometer.⁶ They found that the astronomical lines must arise from one or more molecules other than HC_{11}N . Interestingly, it turned out that the B_0 value predicted by Oka is in considerably better agreement with the microwave data than with the B_0 value determined from the putative astronomical lines. On the basis of the laboratory measurements, two consecutive rotational transitions, $J = 39 \rightarrow 38$ and $38 \rightarrow 37$, could be detected in TMC-1 by means of the 43 m telescope at the National Radio Astronomy Observatory (NRAO).⁷ Making use of an *ab initio* electric dipole moment of 5.47 D as calculated by the author, the column density of HC_{11}N in TMC-1 for a rotational temperature of 10 K was determined to be $2.8 \times 10^{11} \text{ cm}^{-2}$. With respect to

molecular hydrogen, this corresponds to a relative abundance of 3×10^{-11} . This example nicely illustrates the importance of *ab initio* calculations in providing molecular data not easily amenable to experiment.

Among the most exciting progress in radio astronomy during the past two decades has been the detection of several molecules in vibrationally excited states. Cyanoacetylene (HC_3N) is the most prominent molecule thereof. Radio lines of vibrationally excited HC_3N were first found by Clark *et al.*⁸ In 1999, this molecule was observed in as many as 11 different vibrationally excited states in so-called hot molecular cores,⁹ which are considered to be centres of star formation. HC_3N thus constitutes a molecular probe for highly excited gas in interstellar clouds and circumstellar envelopes.

In the laboratory, rotational transitions within vibrationally excited states appear as so-called vibrational satellites of the corresponding ground-state rotational transitions and, in relation to the latter, are characterised by vibration–rotation coupling constants, α_r , and, for transitions within degenerate vibrational states, l -type doubling constants, potentially also higher-order spectroscopic constants. For smaller semirigid molecules, vibration–rotation and l -type doubling constants are easily amenable to computation by standard *ab initio* methods. As long as the vibrational amplitudes are small, second-order perturbation theory in normal coordinate space (see, *e.g.*, ref. 10) performs very well. This approach requires the knowledge of the equilibrium structure of the molecule under consideration, the nuclidic masses and the full set of quadratic and cubic force constants which are usually combined in the term “cubic force field”. Present day high-level *ab initio* calculations may yield very accurate cubic force fields, with relative errors in the most significant terms of the order of 1%. Particularly successful have been calculations employing the coupled cluster variant CCSD(T)¹¹ which combines cost-effectiveness and accuracy and may nowadays be handled on inexpensive personal computers, at least for molecules with fewer than ten atoms.

Interestingly, isomers have been detected by radio astronomy for a few of the known interstellar molecules. These observations may give some hint to the ways of chemical synthesis. A well-known example is provided by HCN and HNC, both of which may be produced through dissociative

recombination of the common cation HCNH^+ with an electron. In the case of cyanoacetylene, two isomers— HC_2NC and HNC_3 —could be detected in TMC-1.^{12,13} In both cases, theoretical work by the author and his coworkers^{14–16} was helpful in the characterisation of the two species.

The interstellar precursor of HC_3N may be HC_3NH^+ , although fast reactions involving only neutral species may also contribute to its formation.¹⁷ This cation is the largest ion which has been observed by radio astronomy so far. In 1992 and 1993, two radio lines attributed to the $J = 5-4$ and $J = 4-3$ rotational transitions of HC_3NH^+ were detected in TMC-1 with the Nobeyama 45 m radio telescope.¹⁸ Making use of the theoretical value for the electric dipole moment of 1.75 D as provided by the author,¹⁹ the column density of HC_3NH^+ in TMC-1 was determined to be $1.0(2) \times 10^{12} \text{ cm}^{-2}$. Compared to the abundance of HC_3N in the same astronomical source, HC_3NH^+ is thus less abundant by a factor of *ca.* 200.

Substantial current interest is devoted to pure carbon clusters. So far, only two polyatomic chains, C_3 and C_5 , could be unambiguously detected in the interstellar medium. The $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition of C_3 at 4051.6 Å has been known to astronomers for more than a century through the analysis of comet spectra. The absorption has been seen strongly in carbon-rich planetary nebulae^{20,21} and was recently found in diffuse interstellar clouds towards various reddened stars.^{22,23} In the infrared and far-infrared, C_3 was observed either through its antisymmetric stretching vibration (ν_3) or its low-frequency bending mode (ν_2).^{24–26} Linear C_5 , which also possesses no permanent dipole moment, could be observed in IRC+10216 through its ν_3 band, which corresponds to the fundamental vibration with highest wavenumber.²⁷ During the past few years there has been some speculation whether longer pure carbon chains might be observable in the ISM by satellite-based far-infrared spectroscopic techniques through low-lying bending vibrations.

Owing to continuous progress in hardware technology, method and computer programme development, theoretical chemistry has become able to make rather accurate predictions for molecules of interest to astrochemistry. In a compact form, the present paper reports the results of *ab initio* calculations on (potential) interstellar molecules carried out by the author in the course of the last five years. The article is more a status report than a review; in particular it should provide the reader with some impression how current theory may assist laboratory spectroscopists and astronomers in their efforts to investigate molecules of interest to interstellar cloud chemistry.

2. Cyanopolynes (HC_{2n+1}N): prominent chains in the interstellar medium

2.1. Equilibrium structures and electric dipole moments

Over the past decade, the author and his coworkers have established accurate equilibrium structures for the cyanopolynes with $n = 1-4$. In the case of linear cyanoacetylene (HC_3N), which is a ubiquitous species in dense interstellar clouds, a mixed experimental/theoretical equilibrium structure could be determined.²⁸ It was obtained through combination of experimental ground-state rotational constants (B_0) for six different isotopomers with the corresponding differences $B_e - B_0$, which were calculated *ab initio* by means of the formula

$$B_e - B_0 \approx \frac{1}{2} \sum_r \alpha_r d_r \quad (1)$$

Here, the vibration–rotation coupling constants α_r describe the variation of the rotational constants upon vibrational excitation to first order and d_r is a degeneracy factor (1 for stretching vibrations and 2 for bending vibrations).

For the larger cyanopolynes up to HC_9N , all of which correspond to fairly normal semirigid molecules, accurate equilibrium geometries were predicted by applying corrections to the equilibrium bond lengths calculated by CCSD(T).^{29–31} The results are summarized in Fig. 1. Throughout, the equilibrium bond lengths are expected to be accurate to better than 0.001 Å.

Due to refinements in instrumental sensibility and production technique, the singly ^{13}C substituted isotopomers of HC_{11}N as well as $\text{HC}_{11}^{15}\text{N}$ could be observed by FTMW spectroscopy in natural abundance.³² In addition, rotational spectra of DC_{11}N were obtained starting from a mixture of fully deuterated diacetylene and cyanoacetylene. Making use of ground-state rotational constants for 14 different isotopic species, an effective (r_0) structure was derived which is given in Table 1. This table includes the results of the author's CCSD(T) calculations for HC_{11}N which were carried out with the MOLPRO suite of programs.^{33,34} Dunning's correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis set³⁵ was employed in the calculations. Table 1 also includes a recommended equilibrium structure which involves corrections to the CCSD(T) equilibrium bond lengths of -0.0018 Å (CH), -0.0064 Å ($\text{C}\equiv\text{C}$), -0.0060 Å (C–C) and -0.0069 Å ($\text{C}\equiv\text{N}$) as established earlier.^{29,30} The present recommended equilibrium structure is in rather close agreement with the experimental r_0 structure, mostly within the statistical uncertainties (1σ) of the

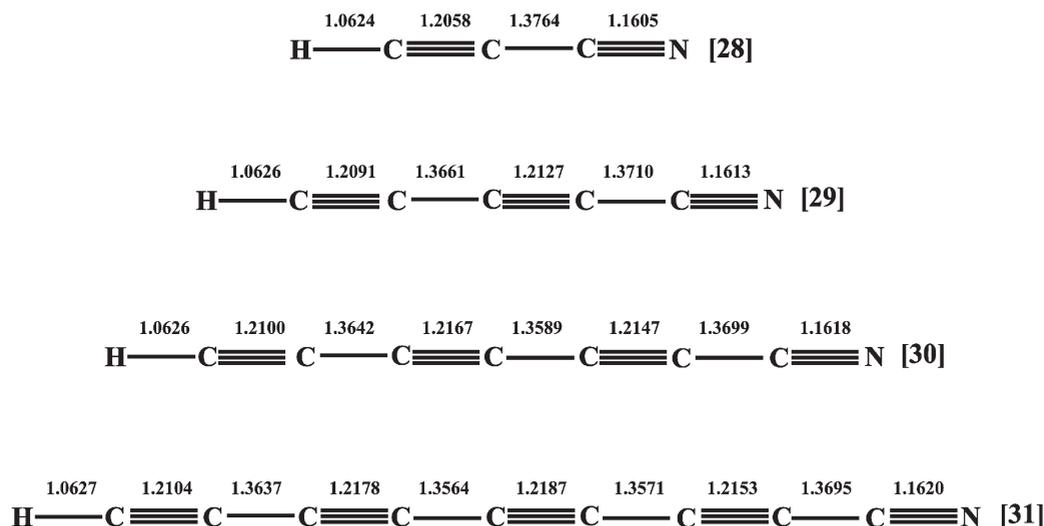


Fig. 1 Recommended equilibrium structures for cyanopolynes, HC_{2n+1}N ($n = 1-4$).

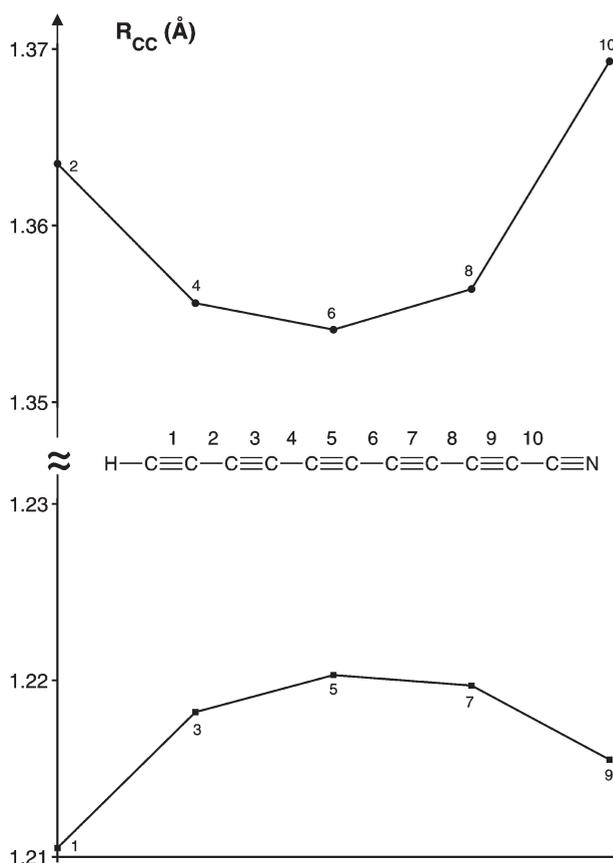
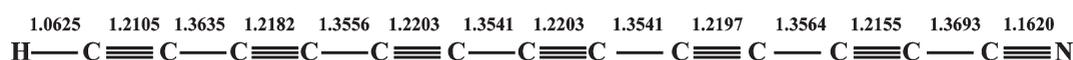
Table 1 Geometric structures for linear HC₁₁N

| | r_0 structure ^a | CCSD(T)/ cc-pVTZ | r_e structure (recommended) |
|---|---------------------------------|---------------------|----------------------------------|
| r (HC ₁₁)/Å | 1.057(1) | 1.0643 | 1.0625 |
| R_1 (C ₁ C ₂)/Å | 1.210(1) | 1.2169 | 1.2105 |
| R_2 (C ₂ C ₃)/Å | 1.360(1) | 1.3695 | 1.3635 |
| R_3 (C ₃ C ₄)/Å | 1.218(2) | 1.2246 | 1.2182 |
| R_4 (C ₄ C ₅)/Å | 1.351(3) | 1.3616 | 1.3556 |
| R_5 (C ₅ C ₆)/Å | 1.217(5) | 1.2267 | 1.2203 |
| R_6 (C ₆ C ₇)/Å | 1.360(8) | 1.3601 | 1.3541 |
| R_7 (C ₇ C ₈)/Å | 1.219(6) | 1.2261 | 1.2197 |
| R_8 (C ₈ C ₉)/Å | 1.350(3) | 1.3624 | 1.3564 |
| R_9 (C ₉ C ₁₀)/Å | 1.217(2) | 1.2219 | 1.2155 |
| R_{10} (C ₁₀ C ₁₁)/Å | 1.365(1) | 1.3753 | 1.3693 |
| R_{11} (C ₁₁ N)/Å | 1.161(1) | 1.1689 | 1.1620 |

^a Ref. 32. Statistical uncertainties (1σ) in terms of the last significant digit are given in parentheses.

latter. This is due to the fact that the zero-point vibrational contributions to the rotational constants (ΔB_0) are quite small in the series of cyanopolynes. Making use of the recommended equilibrium structure for HC₁₁N from this work, the equilibrium rotational constant is obtained as $B_e = 168.675$ MHz. The ratio $B_0(\text{exp.})/B_e(\text{theor.})$ is 1.0023 and thus rather close to unity.

The individual C–C equilibrium bond lengths of HC₁₁N are displayed graphically in Fig. 2. Those in the middle of the

**Fig. 2** Comparison of carbon–carbon equilibrium bond lengths for HC₁₁N (CCSD(T)/cc-pVTZ + corrections).**Fig. 3** Recommended equilibrium structure for HC₁₃N (see the text).**Table 2** Calculated equilibrium electric dipole moments (μ_e/D) for cyanopolynes HC_{2n+1}N^a

| n | SCF | MP2 | CCSD | CCSD-T | CCSD(T) |
|-----|--------|--------|--------|--------|---------|
| 1 | -4.178 | -3.782 | -3.821 | -3.781 | -3.783 |
| 2 | -4.882 | -4.409 | -4.427 | -4.409 | -4.411 |
| 3 | -5.431 | -4.923 | -4.892 | -4.909 | -4.910 |
| 4 | -5.855 | -5.343 | -5.247 | -5.305 | -5.305 |
| 5 | -6.181 | -5.683 | -5.518 | -5.618 | -5.618 |

^a Basis set: aug-cc-pVTZ. Sign of dipole moment corresponds to polarity $^{\delta+}\text{HC}_{2n+1}\text{N}^{\delta-}$. Throughout, the calculations were carried out at the recommended equilibrium structure (*cf.* Fig. 1 and Table 1).

molecule appear to have essentially converged. We may thus predict the equilibrium structures of larger cyanopolynes by adding one or more mid-term C₂ links with geometrical parameters of 1.3541 Å and 1.2203 Å, respectively. Fig. 3 shows the results for HC₁₃N as an example. The corresponding B_e value is 106.700 MHz, again slightly smaller than the experimental B_0 value of 106.97258(4) MHz.³⁶

At the recommended equilibrium structures from Fig. 1 and Table 1, electric dipole moments (μ_e) have been calculated. The flexible aug-cc-pVTZ basis³⁷ was used in conjunction with five different methods. Results of the calculations are given in Table 2. Practically identical results are obtained by the two coupled cluster variants including connected triple substitutions, CCSD(T)¹¹ and CCSD-T.³⁸ They provide the most reliable values from this work. Experimentally, a precise ground-state dipole moment has been determined for HC₃N: $\mu_0 = (-)3.73172(1)$ D.³⁹ It differs from the present μ_e values as obtained by CCSD-T or CCSD(T) by 0.05 D. Compared to HC₃N, the experimental μ_0 value for HC₅N of $(-)4.33(5)$ D⁴⁰ has a considerably larger standard deviation and so no proper comparison with the present μ_e values is possible. The accurate calculation of the differences $\mu_0 - \mu_e$ is still a tedious task for polyatomic molecules and no attempts in this direction have been undertaken in the present work.

2.2. Spectroscopic constants of cyanoacetylene (HC₃N)

Mainly owing to its astrochemical significance, HC₃N has been studied by spectroscopists in great detail and a rather thorough comparison between experiment and theory is therefore possible. A complete cubic force field has been calculated by the author using the CCSD(T) method and Dunning's cc-pVQZ basis³⁵ set which comprises 250 contracted Gaussian-type orbitals (cGTOs). Therefrom, various spectroscopic constants have been calculated for HC₃N and its isotopomers by standard perturbation theory in normal coordinate space. Those constants obtained for the most abundant species are compared with the corresponding experimental data in Table 3.

The calculated harmonic vibrational wavenumbers (ω_r) should have uncertainties not exceeding a few cm⁻¹. No reliable experimental values are available at present. This is not surprising for a penta-atomic molecule, however, since the proper determination of ω_r values through spectroscopic measurements requires a great knowledge on overtones, combination tones and potential perturbations between different vibrational states. Among the vibration–rotation coupling constants (α_r) excellent agreement between theory and

Table 3 Harmonic vibrational wavenumbers, vibration–rotation coupling constants, *l*-type doubling constants and quartic centrifugal distortion constants for HC₃N

| Spectroscopic constant | CCSD(T) | | Spectroscopic constant | CCSD(T) | |
|---------------------------|---------|-------------------|------------------------|---------|--------------------|
| | CCSD(T) | Exp. ^a | | CCSD(T) | Exp. ^a |
| ω_1/cm^{-1} | 3452 | | α_5/MHz | -1.714 | -1.563 |
| ω_2/cm^{-1} | 2316 | | α_6/MHz | -9.233 | -9.256 |
| ω_3/cm^{-1} | 2111 | | α_7/MHz | -14.389 | -14.455 |
| ω_4/cm^{-1} | 879 | | q_5/MHz | 2.419 | 2.538 |
| ω_5/cm^{-1} | 671 | | q_6/MHz | 3.498 | 3.582 |
| ω_6/cm^{-1} | 501 | | q_7/MHz | 6.394 | 6.538 |
| ω_7/cm^{-1} | 223 | | q_5^r/Hz | -1.052 | -1.331 |
| α_1/MHz | 7.030 | 7.331 | q_6^r/Hz | -1.770 | -2.063 |
| α_2/MHz | 21.589 | 21.572 | q_7^r/Hz | -15.516 | -16.291 |
| α_3/MHz | 13.767 | 13.895 | D_e^l/kHz | 0.506 | 0.544 ^b |
| α_4/MHz | 10.447 | 11.100 | | | |

^a Refs. 41 and 42. ^b Ground-state value.

experiment is observed for those fundamentals which appear to be essentially unperturbed (ν_7 , ν_6 , ν_3 and ν_2). Deperturbed experimental values are quoted for α_5 and α_4 , but the applied deperturbation procedures may still not be sufficiently complete to allow for precise comparison. Nevertheless, the differences in calculated and experimental α_5 and α_4 values do not exceed 10% which is already quite reasonable for a molecule of the size of HC₃N. The *l*-type doubling constants q_l were calculated from the quadratic force field, the equilibrium geometry and the nuclidic masses. For linear molecules, this procedure tends to underestimate the *l*-type doubling constants by a few per cent with respect to accurate experimental data. Such a situation is also observed for HC₃N, where the theoretical values for q_7 and q_6 differ from experiment by 2%. The larger difference of 5% for q_5 may have to do with the perturbations which affect the $\nu_5 = 1$ vibrational state. Even quite good agreement between theory and experiment is observed for the very small constants q_l^r which describe the rotational dependence of *l*-type doubling. In particular, agreement between theory and experiment for the lowest bending vibration ν_7 is very good. As is usually observed for linear molecules (see, *e.g.*, ref. 43), the calculated equilibrium centrifugal distortion constants, termed D_e^l , are smaller than the corresponding ground-state values. Here, the ratio $D_0^l(\text{exp.})/D_e^l(\text{theor.})$ is 1.075.

2.3. Isomers of cyanoacetylene: HCCNC, HNC₃ and HCNCC

In the course of a molecular line survey towards TMC-1 within the 45 m Nobeyama radio telescope in 1985 and 1986, two lines were found at 49 677.9 and 39 742.6 MHz which could not be assigned to transitions of known molecules. The situation changed when Dreizler and coworkers succeeded in measuring the microwave spectrum of HCCNC (isocyanoacetylene) which was synthesized through flash vacuum pyrolysis of either Cr(CO)₅CN–CCl=CHCl or Cr(CO)₅CN–CCl₂–CHCl₂.⁴⁴ The ground-state rotational constant was derived as 4967.8370(3) MHz, quite close to the prediction of 4964 MHz made earlier by Botschwina and Sebald on the basis of SCF calculations for the equilibrium bond lengths plus empirical corrections.¹⁴ With the microwave data at hand, the radio astronomical lines could be readily assigned to the $J = 4 - 3$ and $J = 5 - 4$ transitions of HCCNC; in addition, a radio line at 89419.4 MHz observed already in 1984 could be attributed to the same species.

Following earlier work employing the coupled electron pair approximation (CEPA),¹⁶ a complete cubic force field was calculated for HCCNC by means of CCSD(T) with the cc-pVQZ basis set.³⁵ It corresponds to an expansion of the potential energy for the vibrational motions of the nuclei around their

equilibrium positions and is given in the form

$$V - V_e = \sum_{ijklmno} C_{ijklmno} \Delta r^i \Delta R_1^j \Delta R_2^k \Delta R_3^l \alpha^m \beta^n \gamma^o. \quad (1)$$

Here, Δr , ΔR_1 , ΔR_2 and ΔR_3 are the changes in the CH, C₍₁₎C₍₂₎, C₍₂₎N and NC₍₃₎ bond lengths with respect to their equilibrium values and angles α , β and γ describe the deviations from linearity in order HC₍₁₎C₍₂₎, C₍₁₎C₍₂₎N and C₍₂₎NC₍₃₎. Two of these angles are defined to have the same sign for a *cis*-like distortion of the nuclear framework. Torsional coordinates are not required as these do not contribute to the cubic force field. The expansion coefficients $C_{ijklmno}$ are listed in Table 4 which includes the calculated equilibrium bond lengths in a footnote.

Calculated and experimental spectroscopic constants for HCCNC and DCCNC are given in Table 5. Most of the experimental data for HCCNC were taken from a recent paper by Vigouroux *et al.*⁴⁵ which reports a global rovibrational analysis of several hundred transitions between more than 100 vibrational states up to energies of about 1900 cm⁻¹. Experimental harmonic wavenumbers are available for ω_4 – ω_7 of the most abundant species,⁴⁵ but these are rather approximate since not all relevant anharmonicity constants could be included in the analysis. Experimental values in parentheses are anharmonic vibrational wavenumbers (see Table 2 of ref. 46); ν_4 is an effective value whereas ν_6 and ν_7 have been extrapolated. The ratios $\omega_i(\text{theor.})/\nu_i(\text{exp.})$ for $i = 1$ are 1.037 and 1.028 for HCCNC and DCCNC, respectively. While the stretching vibration with highest wavenumber in HCCNC corresponds to a rather well localized CH oscillator, the corresponding vibration of DCCNC (both harmonic and anharmonic) bears significant heavy-atom stretching contributions.

The lowest bending vibrational states ($\nu_7 = 1$) of either HCCNC or DCCNC are energetically well separated from all other vibrational states and thus clearly unperturbed. Very good agreement between theory and experiment is observed for all of their spectroscopic constants given in Table 5. For HCCNC, the vibration–rotation coupling constant α_7 differs by 2.2% and the calculated *l*-type doubling constant q_7^e is smaller than the corresponding experimental value by 2.8%. Even for the small q_7^r constant, theory and experiment differ by only 5%. Practically the same situation holds for DCCNC. The present CCSD(T) values for α_6 and q_6^e of HCCNC and DCCNC are in very close agreement with the corresponding experimental data. This may well be expected since the $\nu_6 = 1$ states should be essentially unperturbed. There is still reasonable agreement for q_6^e of DCCNC (–2.792 Hz vs. (–)4.292 Hz), but the corresponding theoretical value for HCCNC of –3.819 Hz differs from the experimental one by a factor of three. The latter appears to be unusually large. It may be noted that very good agreement between theory and experiment was obtained for q_6^e of HC₃N.

The $\nu_5 = 1$ state appeared to be slightly perturbed in both millimetre-wave and infrared spectra. This perturbation results from anharmonic interaction with the $3\nu_7^1$ state. The experimental rotational diagonal parameter of ref. 45 is –2.562(1) MHz and may be directly compared to the present α_5 value of –2.642 MHz. The present q_5 value of 3.025 MHz is smaller than the corresponding experimental value by 5%.

Like for cyanoacetylene, the $\nu_4 = 1$ states of HCCNC and DCCNC are heavily perturbed. In their vibrational analysis of states lying in the region 828–955 cm⁻¹, Vigouroux *et al.*⁴⁵ decided to fix α_4 at our earlier CEPA-1 value,¹⁶ which is very close to the current CCSD(T) result. For DCCNC, the present value for α_4 is larger than the deperturbed experimental one⁴⁶ by 8%.

The states $\nu_3 = 1$ and $\nu_2 = 1$ of both HCCNC and DCCNC appear to be free of perturbations. Excellent agreement between theory and experiment is observed for all α_r values ($r = 2, 3$), with differences of less than 0.5%. Likewise, calculated and experimental α_1 value for DCCNC differ by

Table 4 CCSD(T)/cc-pVQZ (valence electrons correlated) cubic force field for HCCNC^a

| Term ^b | | | | | Term ^b | | | | | | | |
|-------------------|----------|----------|----------|-----------|-------------------|----------|----------|----------|----------|----------|----------|-----------|
| <i>i</i> | <i>j</i> | <i>k</i> | <i>l</i> | Value/au | <i>i</i> | <i>j</i> | <i>k</i> | <i>l</i> | <i>m</i> | <i>n</i> | <i>o</i> | Value/au |
| 2 | 0 | 0 | 0 | 0.205219 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0.025349 |
| 3 | 0 | 0 | 0 | -0.204422 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0.040411 |
| 0 | 2 | 0 | 0 | 0.518302 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0.022651 |
| 0 | 3 | 0 | 0 | -0.535350 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0.027717 |
| 0 | 0 | 2 | 0 | 0.267724 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | -0.001493 |
| 0 | 0 | 3 | 0 | -0.276151 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0.003991 |
| 0 | 0 | 0 | 2 | 0.502651 | 1 | 0 | 0 | 0 | 2 | 0 | 0 | -0.008692 |
| 0 | 0 | 0 | 3 | -0.597685 | 1 | 0 | 0 | 0 | 0 | 2 | 0 | -0.002601 |
| 1 | 1 | 0 | 0 | -0.007097 | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 0.000483 |
| 1 | 0 | 1 | 0 | -0.001107 | 0 | 1 | 0 | 0 | 2 | 0 | 0 | -0.053818 |
| 1 | 0 | 0 | 1 | 0.000411 | 0 | 1 | 0 | 0 | 0 | 2 | 0 | -0.069194 |
| 0 | 1 | 1 | 0 | 0.038031 | 0 | 1 | 0 | 0 | 0 | 0 | 2 | 0.004576 |
| 0 | 1 | 0 | 1 | -0.025939 | 0 | 0 | 1 | 0 | 2 | 0 | 0 | 0.005774 |
| 0 | 0 | 1 | 1 | 0.032788 | 0 | 0 | 1 | 0 | 0 | 2 | 0 | -0.041831 |
| 2 | 1 | 0 | 0 | 0.005503 | 0 | 0 | 1 | 0 | 0 | 0 | 2 | -0.042304 |
| 1 | 2 | 0 | 0 | -0.001428 | 0 | 0 | 0 | 1 | 2 | 0 | 0 | -0.004789 |
| 2 | 0 | 1 | 0 | 0.000237 | 0 | 0 | 0 | 1 | 0 | 2 | 0 | 0.007445 |
| 1 | 0 | 2 | 0 | 0.000112 | 0 | 0 | 0 | 1 | 0 | 0 | 2 | -0.051282 |
| 2 | 0 | 0 | 1 | -0.000244 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | -0.000287 |
| 1 | 0 | 0 | 2 | -0.000294 | 1 | 0 | 0 | 0 | 1 | 0 | 1 | 0.000083 |
| 0 | 2 | 1 | 0 | -0.007433 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | -0.000044 |
| 0 | 1 | 2 | 0 | -0.051507 | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 0.039605 |
| 0 | 2 | 0 | 1 | -0.002697 | 0 | 1 | 0 | 0 | 1 | 0 | 1 | -0.002087 |
| 0 | 1 | 0 | 2 | -0.008667 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 0.007958 |
| 0 | 0 | 2 | 1 | -0.067008 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | -0.000219 |
| 0 | 0 | 1 | 2 | 0.002047 | 0 | 0 | 1 | 0 | 1 | 0 | 1 | 0.000746 |
| 1 | 1 | 1 | 0 | -0.001373 | 0 | 0 | 1 | 0 | 0 | 1 | 1 | -0.003656 |
| 1 | 1 | 0 | 1 | 0.000182 | 0 | 0 | 0 | 1 | 1 | 1 | 0 | -0.000907 |
| 1 | 0 | 1 | 1 | -0.000118 | 0 | 0 | 0 | 1 | 1 | 0 | 1 | 0.004004 |
| 0 | 1 | 1 | 1 | 0.050318 | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0.009622 |

^a CCSD(T)/cc-pVQZ equilibrium geometry: $r_c(\text{CH}) = 1.0630 \text{ \AA}$, $R_{1c}(\text{C}_{(1)}\text{C}_{(2)}) = 1.2063 \text{ \AA}$, $R_{2c}(\text{C}_{(2)}\text{N}) = 1.3177 \text{ \AA}$, and $R_{3c}(\text{NC}_{(3)}) = 1.1822 \text{ \AA}$.^b See eqn. (1) for definition.**Table 5** Harmonic vibrational wavenumbers, vibration–rotation coupling constants, *l*-type doubling constants and quartic centrifugal distortion constants for HCCNC and DCCNC

| | HCCNC | | DCCNC | |
|---------------------------|---------|-----------------------|---------|--------------------|
| | CCSD(T) | exp. ^a | CCSD(T) | exp. ^a |
| ω_1/cm^{-1} | 3464 | (3339) | 2691 | (2618) |
| ω_2/cm^{-1} | 2262 | (2219) | 2196 | (2158) |
| ω_3/cm^{-1} | 2067 | (2037) | 1994 | (1965) |
| ω_4/cm^{-1} | 941 | 938 | 924 | (929) |
| ω_5/cm^{-1} | 627 | 617 | 482 | (480) |
| ω_6/cm^{-1} | 432 | 430 | 430 | (425) |
| ω_7/cm^{-1} | 211 | 208 | 204 | (200) |
| α_1/MHz | 8.214 | 8.442 | 13.099 | 13.077 |
| α_2/MHz | 24.012 | 23.901 | 20.150 | 20.143 |
| α_3/MHz | 15.360 | 15.308 | 12.561 | 12.583 |
| α_4/MHz | 11.967 | (11.880) ^b | 10.386 | 9.623 ^c |
| α_5/MHz | -2.642 | -2.562 | -5.117 | -4.971 |
| α_6/MHz | -10.518 | -10.717 | -9.482 | -9.447 |
| α_7/MHz | -15.444 | -15.785 | -13.704 | -13.898 |
| q_5/MHz | 3.025 | 3.193 | 3.314 | 3.423 |
| q_6/MHz | 4.499 | 4.576 | 3.902 | 3.997 |
| q_7/MHz | 8.061 | 8.289 | 7.122 | 7.330 |
| q_5^l/Hz | -1.542 | -3.811 | -2.275 | -2.579 |
| q_6^l/Hz | -3.819 | -11.294 | -2.792 | -4.292 |
| q_7^l/Hz | -22.120 | -23.311 | -17.819 | -19.269 |
| D_c^J/kHz | 0.579 | 0.627 ^d | 0.477 | 0.517 ^d |

^a Refs. 45–48. Anharmonic values are given in parentheses. ^b The CEPA-1 value of ref. 16 was used in the global rovibrational analysis (ref. 45). ^c Deperturbed value (ref. 46). ^d Ground-state values.

only 0.2%. There is a 2.7% difference in α_1 of HCCNC. This may be indicative of some slight perturbation of unknown nature. On the other hand, one cannot rule out that second order perturbation theory works less well for ν_1 of HCCNC in comparison to ν_1 of the deuterated species since the CH stretching vibration of the normal species has the larger vibrational amplitude.

After the detection of HCCNC, Kawaguchi and coworkers were able to identify another isomer of cyanoacetylene in TMC-1, namely HNC₃.¹³ In the ISM, it may be produced from the same precursor ion, protonated cyanoacetylene (HC₃NH⁺), through dissociative recombination with an electron. The observed lines in TMC-1 occurred at frequencies of 28009.975, 37346.556 and 46683.086 MHz and were assigned to rotational transitions 3–2, 4–3 and 5–4, respectively. The assignment was supported by laboratory millimetre-wave spectroscopy in a cooled free-space cell. Furthermore, the FTMW spectrum of HNC₃ was observed at the University of Tokyo and the $J = 2-1$ and $1-0$ transitions were detected with resolved hyperfine structure.⁴⁹ Both radio astronomical and laboratory data were analysed with the formula for a linear molecule, yielding ground-state rotational and centrifugal distortion constants of $B_0 = 4668.33541(51)$ MHz and $D_0 = 0.61834(36)$ kHz, with 1σ in parentheses. These data do not tell us much about the geometric structure of this high-energy isomer of cyanoacetylene. Making use of the CEPA method, the author and his coworkers¹⁶ found that the equilibrium structure of HNC₃ is bent, with the HNC equilibrium bond angle of 136° differing substantially from linearity. Since the calculated barrier height is as small as 469 cm⁻¹, HNC₃ must be classified as a quasi-linear molecule.

Table 6 Calculated equilibrium structures for all-*trans* HNC₃

| Geometrical parameter | CEPA-1 ¹⁶ | B3LYP ⁵² | B3LYP ⁵⁰ | CCSD(T)/cc-pVQZ | Recommended |
|---|----------------------|---------------------|---------------------|-----------------|-------------|
| $r_e(\text{NH})/\text{\AA}$ | 1.0038 | 1.009 | 1.005 | 1.0011 | 0.9992(5) |
| $R_{1e}(\text{NC}_{(1)})/\text{\AA}$ | 1.1928 | 1.203 | 1.188 | 1.1894 | 1.1862(5) |
| $R_{2e}(\text{C}_{(1)}\text{C}_{(2)})/\text{\AA}$ | 1.3076 | 1.314 | 1.302 | 1.3084 | 1.3044(8) |
| $R_{3e}(\text{C}_{(2)}\text{C}_{(3)})/\text{\AA}$ | 1.2745 | 1.285 | 1.268 | 1.2740 | 1.2700(8) |
| $\alpha_e(\text{HNC}_{(1)})/^\circ$ | 136.1 | 137.4 | 140 | 140.22 | 140.2(10) |
| $\beta_e(\text{NC}_{(1)}\text{C}_{(2)})/^\circ$ | 173.8 | 173.4 | 175 | 173.93 | 173.9(4) |
| $\gamma_e(\text{C}_{(1)}\text{C}_{(2)}\text{C}_{(3)})/^\circ$ | 175.0 | 178.1 | 178 | 176.57 | 176.6(4) |

A matrix isolation infrared spectrum of HNC₃ was recently reported by Kolos and Sobolewski⁵⁰ who observed the three stretching vibrations with highest wavenumber (ν_1 – ν_3) for three different isotopomers, thereby confirming an earlier tentative assignment of an absorption observed at 2205 cm⁻¹.⁵¹ These experiments do not yield any information on the geometric structure and the degree of floppiness of HNC₃, however. Potential reaction paths for interstellar formation of HNC₃ and other isomers of cyanoacetylene were recently discussed by Osamura *et al.*⁵²

The present work extends our previous paper¹⁶ by reporting results of high-level *ab initio* calculations for the equilibrium structure of HNC₃ and the barrier height to linearity. An accurate calculation of the low-lying bending vibrational states remains a challenge to theoretical chemistry, keeping in mind that no reliable calculations in full dimensionality have yet been performed for any penta-atomic quasilinear molecule. Calculated equilibrium structures for all-*trans* HNC₃ are listed in Table 6, with the results from this work being given in the last two columns. According to the author's experience, the errors in CCSD(T) calculations with the cc-pVQZ basis set are very systematic and suitable corrections have been employed to produce the recommended equilibrium structure, for which estimates of the remaining uncertainties in terms of the least significant digit are given in parentheses.

The remaining six geometrical parameters have been optimised in the range $180^\circ \geq \alpha(\text{HNC}_{(1)}) \geq 120^\circ$. The resulting energy profile is shown in Fig. 4 along with the optimum values of the bond lengths as a function of α . The changes in the optimum values of the bond angles $\beta(\text{NC}_{(1)}\text{C}_{(2)})$ and $\gamma(\text{C}_{(1)}\text{C}_{(2)}\text{C}_{(3)})$ are relatively small; between the energy minimum at $\alpha = 140.2^\circ$ and $\alpha = 120^\circ$ they amount to only 0.6° and 1.0°, respectively. The barrier height to linearity is calculated as 331.6 cm⁻¹, 29% smaller than our previous CEPA value. It is quite similar to the barrier height for HCCN⁵³ which constitutes another quasilinear interstellar molecule.⁵⁴

Very recently, the first spectroscopic evidence of another isomer of cyanoacetylene was obtained. Photolysing cyanoacetylene trapped in an argon matrix at $\lambda > 120$ nm, IR bands at 3277, 2102 and 1920 cm⁻¹ were observed and assigned to stretching vibrations of HCNCC.⁵⁵ These tentative assignments are based on DFT calculations^{55,56} and deuterium substitution. In the present work, the complete cubic force field of HCNCC has been calculated by CCSD(T) with the cc-pVQZ basis set, from which the spectroscopic constants given in Table 7 were obtained. The isomer HCNCC is more flexible than either HC₃N or HCCNC. Its equilibrium structure is still linear, but HCNCC has a relatively shallow HCN bending potential. A recommended equilibrium structure of HCNCC is obtained by applying corrections to the CCSD(T)/cc-pVQZ equilibrium bond lengths. The resulting values are $r_e(\text{CH}) = 1.0627(5)$ Å, $R_{1e}(\text{CN}) = 1.1630(5)$ Å, $R_{2e}(\text{NC}) = 1.2772(10)$ Å and $R_{3e}(\text{CC}) = 1.2652(10)$ Å, with estimated uncertainties in terms of the least significant digit given in parentheses. Throughout, they differ from the values predicted by Kolos and Dobrowolski⁵⁶ by less than 0.001 Å. Combining the B_e value for HCNCC obtained from the present recom-

mended equilibrium structure with the CCSD(T)/cc-pVQZ value for ΔB_0 from Table 7, the ground-state rotational constant of HCNCC is predicted to be 5003.6 MHz. Owing to the higher flexibility of HCNCC compared to the semirigid isomers HC₃N and HCCNC and the larger uncertainties in the equilibrium bond lengths R_{2e} and R_{3e} , the present B_0 prediction may well have an error of the order of 10 MHz or 0.2%.

3. Radicals of type C_{2n+1}N

Besides the closed-shell cyanopolyynes, two of the corresponding radicals of type C_{2n+1}N have been detected in the ISM. The cyanoethynyl radical (C₃N) was found in IRC+10216 already in 1977,⁵⁷ six years prior to its laboratory investigation by millimetre-wave spectroscopy.⁵⁸ It took about twenty years until the next member of the series of cyanopolyyne radicals, C₅N, could be observed in the ISM.

Making use of unrestricted Hartree–Fock (UHF) calculations, the electronic ground state of C₅N was predicted to be of ²Π symmetry and to have a small electric dipole moment,⁵⁹

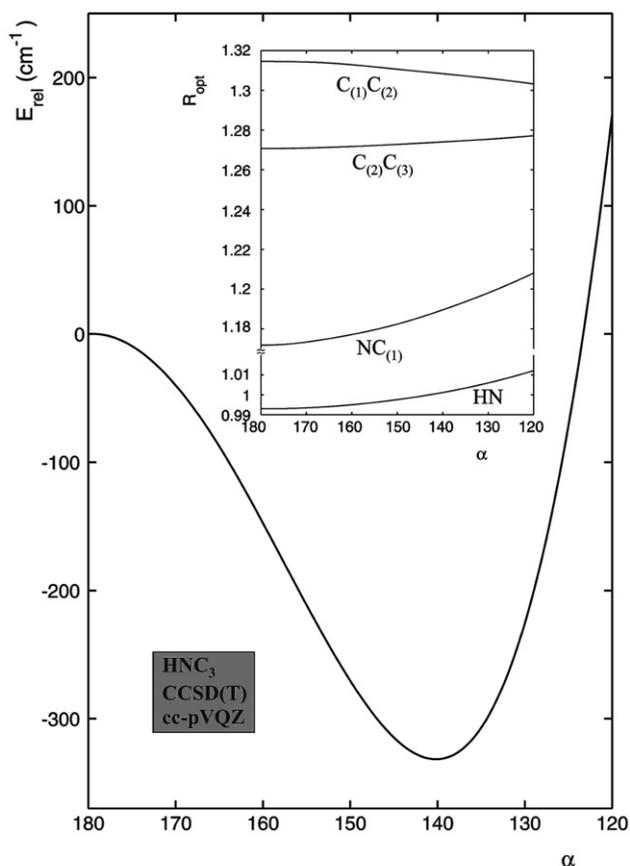


Fig. 4 Minimum energy profile for HNC₃ as a function of the HNC angle α .

Table 7 Harmonic vibrational wavenumbers, vibration–rotation coupling constants, *l*-type doubling constants and quartic centrifugal distortion constants for HCNC and DCNC (CCSD(T)/cc-pVQZ)^a

| | HCNC | DCNC |
|---------------------------|---------|---------|
| ω_1/cm^{-1} | 3451 | 2677 |
| ω_2/cm^{-1} | 2158 | 2078 |
| ω_3/cm^{-1} | 1956 | 1900 |
| ω_4/cm^{-1} | 960 | 945 |
| ω_5/cm^{-1} | 496 | 479 |
| ω_6/cm^{-1} | 307 | 246 |
| ω_7/cm^{-1} | 166 | 159 |
| α_1/MHz | 8.609 | 12.772 |
| α_2/MHz | 24.552 | 25.084 |
| α_3/MHz | 20.563 | 14.169 |
| α_4/MHz | 12.089 | 10.169 |
| α_5/MHz | -6.941 | -6.911 |
| α_6/MHz | -9.928 | -13.516 |
| α_7/MHz | -23.298 | -20.390 |
| $\Delta B_0/\text{MHz}$ | -7.061 | -9.672 |
| q_5/MHz | 4.215 | 3.752 |
| q_6/MHz | 5.550 | 5.984 |
| q_7/MHz | 10.185 | 9.167 |
| q_5^l/Hz | -2.001 | 3.752 |
| q_6^l/Hz | -8.189 | -12.713 |
| q_7^l/Hz | -49.911 | -41.054 |
| D_v^l/kHz | 0.570 | 0.472 |

^a CCSD(T)/cc-pVQZ equilibrium geometry: $r_c(\text{CH}) = 1.0646 \text{ \AA}$, $R_{1c}(\text{CN}) = 1.1662 \text{ \AA}$, $R_{2c}(\text{NC}) = 1.2812 \text{ \AA}$ and $R_{3c}(\text{CC}) = 1.2690 \text{ \AA}$.

quite unfavourable for detection of the radical in the interstellar medium by means of radio astronomy. However, extensive coupled cluster calculations by the author yielded a $^2\Sigma$ state as the electronic ground-state.⁶⁰ Shortly afterwards, the radical was detected by means of FTMW spectroscopy, being generated by a discharge in a mixture of HC_5N and HC_3N diluted in argon and subsequently cooled down to a few kelvin in a supersonic free jet expansion.⁶¹ The ground-state rotational constant was determined to be $1403.07981(54) \text{ MHz}$, 6 MHz above the predicted equilibrium rotational constant.⁶⁰ This difference is relatively large for a linear molecule of the given sort and may be indicative of vibronic interaction between the $^2\Sigma$ and $^2\Pi$ states.

The first radio astronomical detection of C_5N was reported in 1998.⁶² Making use of the 100 m Effelsberg telescope, the $N = 9 \rightarrow 8$ rotational transition was observed towards TMC-1. The $N = 9-8$ line was found to be split into two fine structure components separated by $10.71 \pm 0.01 \text{ MHz}$, very close to the spin–rotation constant measured earlier in the laboratory by Kasai *et al.*⁶¹ The abundance of C_5N in TMC-1 was determined with the aid of the author's calculated dipole moment of $\mu_e = -3.385 \text{ D}$;⁶⁰ with respect to molecular hydrogen it is as low as 3×10^{-11} .

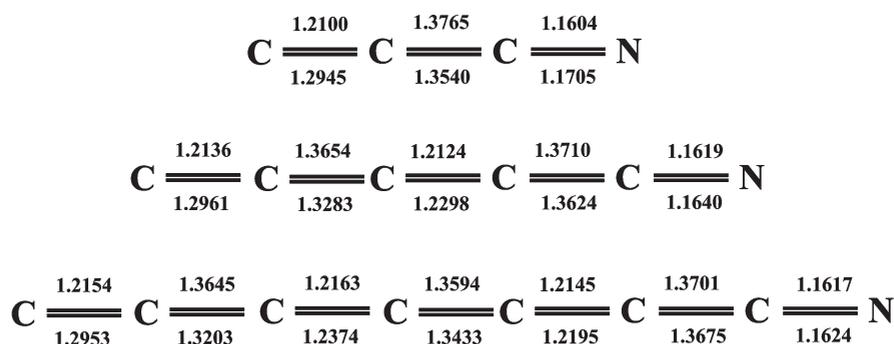


Fig. 5 Recommended equilibrium structures for the $^2\Sigma$ states (top) and $^2\Pi$ states (bottom) of cyanopolyne radicals, C_{2n+1}N ($n = 1-3$).

A summary of theoretical work on C_{2n+1}N radicals as carried out at Göttingen is given in Fig. 5 and Tables 8 and 9. The figure shows recommended equilibrium structures for the $^2\Sigma$ and $^2\Pi$ states of C_3N , C_5N and C_7N which are based on calculations employing partially restricted coupled cluster theory, variant RCCSD(T).⁶³

Calculated equilibrium excitation energies for the $^2\Pi$ states, termed T_e , are listed in Table 8. Inclusion of electron correlation effects is mandatory to arrive at meaningful results. The importance of connected triple substitutions increases strongly with increasing chain lengths. They have very little influence on the T_e value of C_3N , but lead even to a change of sign of T_e in the case of C_7N . Owing to the small energetic separation between $^2\Sigma$ and $^2\Pi$ states for C_5N and C_7N , vibronic effects may play an important role for an accurate calculation of frequencies and intensities of transitions between individual rovibrational states within the two electronic states.

Calculated equilibrium dipole moments for the $^2\Sigma$ and $^2\Pi$ states of cyanopolyne radicals up to C_7N are listed in Table 9. Throughout, electron correlation changes the sign of μ_e of the $^2\Pi$ states. Connected triple substitutions provide significant contributions to the μ_e values of these states while their influence on the dipole moments of the $^2\Sigma$ states is rather minor, not exceeding 0.04 D in all the three cases presented in Table 9.

On the basis of the author's predictions, a rather extensive search for the rotational spectrum of C_7N was recently carried

Table 8 Calculated equilibrium excitation energies (in cm^{-1}) for the $^2\Pi$ states of radicals of type C_{2n+1}N ($n = 1-3$)^a

| <i>n</i> | RHF | RCCSD | RCCSD-T | RCCSD(T) |
|----------|------|-------|---------|----------|
| 1 | 508 | 2320 | 2285 | 2316 |
| 2 | -324 | 698 | 455 | 491 |
| 3 | -612 | 124 | -357 | -304 |

^a Basis set: cc-pVQZ. Throughout, the calculations were carried out at the recommended equilibrium structures of Fig. 5.

Table 9 Calculated equilibrium dipole moments (in D) for radicals of type C_{2n+1}N ^a

| Radical | State | RHF | RCCSD | RCCSD-T | RCCSD(T) |
|----------------------|--------------|--------|--------|---------|----------|
| C_3N | X $^2\Sigma$ | -3.255 | -2.901 | -2.865 | -2.867 |
| | A $^2\Pi$ | -0.551 | 0.046 | 0.200 | 0.200 |
| C_5N | X $^2\Sigma$ | -3.865 | -3.423 | -3.409 | -3.412 |
| | A $^2\Pi$ | -0.532 | 0.335 | 0.567 | 0.566 |
| C_7N | X $^2\Pi$ | -0.431 | 0.660 | 0.958 | 0.957 |
| | A $^2\Sigma$ | -4.328 | -3.809 | -3.824 | -3.826 |

^a Basis set: aug-cc-pVTZ. Throughout, the calculations were carried out at the recommended equilibrium structures (*cf.* Fig. 5).

out by McCarthy *et al.*⁶⁴ The absence of lines at the predicted frequencies may be indicative of a small electric dipole moment of the C_7N electronic ground state, in agreement with the author's theoretical work.

4. Cumulenic systems with one hetero end atom

4.1. Linear silicon carbides

Linear silicon carbides SiC_n have large electric dipole moments and are thus favourable candidates for radio astronomy. Indeed, SiC_4 has been observed in IRC + 10 216 about 15 years ago.⁶⁵ Besides diatomic SiC ,⁶⁶ SiC_2 and SiC_3 have been detected in their most stable ring forms.^{67,68}

In a joint experimental/theoretical paper, linear SiC_4 and SiC_6 were characterised through FTMW spectroscopy and coupled cluster calculations.⁶⁹ A full cubic force field was calculated for the former by means of CCSD(T) with the cc-pVQZ basis set.^{35,70} Combining the calculated differences $B_e - B_0$ (*cf.* eqn. (1)) with the experimental B_0 values of seven different isotopomers, the following equilibrium structure could be determined: $R_{1e}(SiC_{(1)}) = 1.6928$ Å, $R_{2e}(C_{(1)}C_{(2)}) = 1.2726$ Å, $R_{3e}(C_{(2)}C_{(3)}) = 1.2986$ Å and $R_{4e}(C_{(3)}C_{(4)}) = 1.2809$ Å. The variance in the CC equilibrium bond lengths does not exceed 0.026 Å and all of them are significantly shorter than in ethene ($R_e = 1.3307$ Å⁷¹). Likewise, the SiC equilibrium bond length is slightly shorter than in $SiCH_2$. Such a situation is characteristic for a hetero-cumulenic system.

While linear silicon carbides with an even number of carbon atoms have closed-shell electronic ground states with $^1\Sigma^+$ symmetry, the ground states of the corresponding chains with an odd number are of $^3\Sigma^-$ symmetry. Nevertheless, as we showed recently for linear SiC_3 and SiC_5 on the basis of RCCD(T) calculations with the cc-pVQZ basis,⁷² the equilibrium bond lengths of the triplet species are rather similar to those of the singlets. For the carbon-carbon equilibrium bond lengths, this is illustrated in Fig. 6. Here, the structures for SiC_3 – SiC_6 were taken from our previous work.^{69,72} For SiC_7 and SiC_8 , new recommended equilibrium structures were established on the basis of (R)CCSD(T) calculations with the cc-pVTZ and cc-pVQZ basis set, respectively. The resulting equilibrium bond lengths (in Å) are:

(a) SiC_7 : 1.7171, 1.2778, 1.2849, 1.2755, 1.2743, 1.2909 and 1.2926.

(b) SiC_8 : 1.7002, 1.2762, 1.2887, 1.2653, 1.2873, 1.2638, 1.2976 and 1.2831.

The corresponding equilibrium rotational constants are 420.98 and 305.97 MHz, respectively. As expected from the previous results for the smaller silicon carbides, they are slightly smaller than the corresponding experimental ground-state rotational constants of 421.08343(4) MHz and 306.26089(4) MHz.⁷³

Over the whole series of molecules, the CC equilibrium bond lengths vary only between 1.264 and 1.303 Å, with the distribution for the triplets being somewhat narrower than for the singlets. The variation in the SiC equilibrium bond lengths extends from 1.693 to 1.731 Å.

(R)CCSD(T) values of the equilibrium dipole moments of SiC_n species are compared in Fig. 7; throughout the aug-cc-pVTZ basis was employed. With the exception of SiC_7 , the data were taken from our previous papers.^{69,72,74} For SiC_7 , $\mu_e = -7.875$ D was obtained which includes a correlation contribution of 12%. An almost linear dependence on n is observed when singlet and triplet states are treated separately; such a behaviour was found earlier for the results of density functional calculations by Ding *et al.*⁷⁵

4.2. C_3S and C_5S

Like the linear silicon carbides, SiC_n , carbon chains with a hetero end atom from the sixth main group of the periodic system

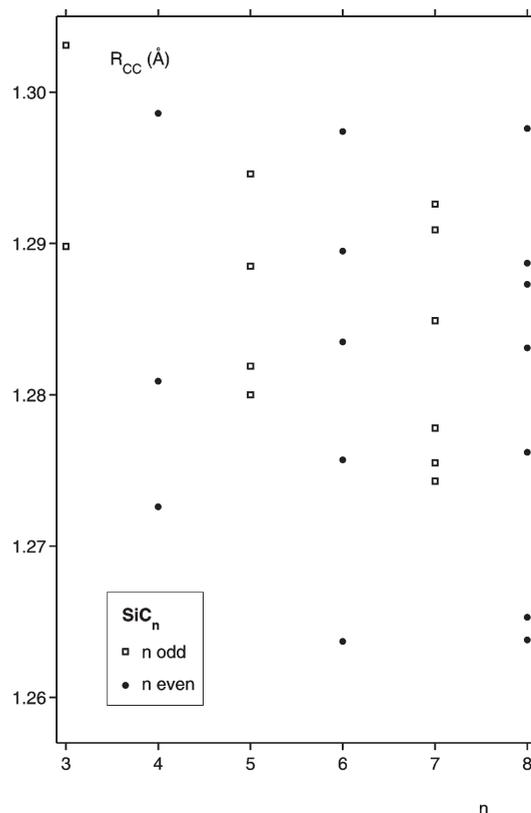


Fig. 6 Distribution of CC equilibrium bond lengths for silicon carbides, SiC_n ($n = 3-8$).

exhibit cumulenic structures. Among closed-shell polyatomic species, rather well-known interstellar molecules of this category are C_3O and C_3S , while only a tentative detection was reported for C_5S . Three strong radio lines at 23 123 40 465

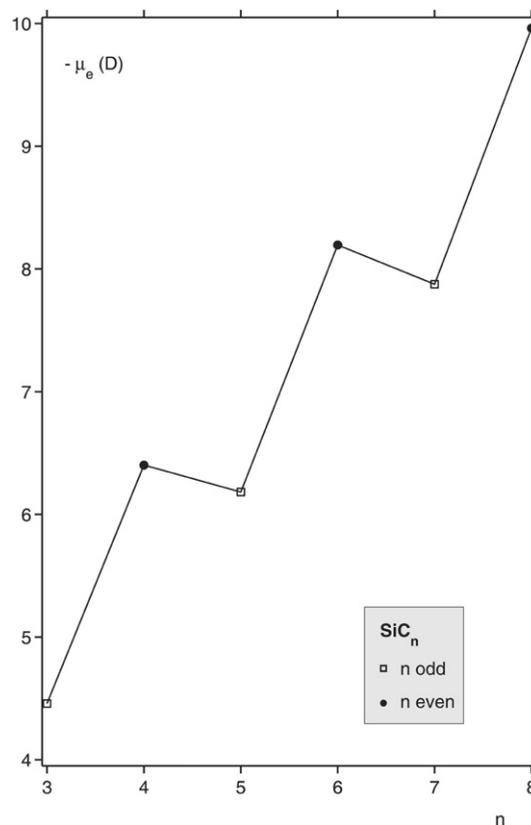


Fig. 7 Equilibrium dipole moments for silicon carbides, SiC_n ($n = 3-8$).

and 46246 MHz detected in TMC-1⁷⁶ were subsequently assigned to the $J = 4-3$, $7-6$ and $8-7$ rotational transitions of linear C₃S on the basis of laboratory microwave data.⁷⁷ Later observations showed that this species is surprisingly abundant in this astronomical source.⁷⁸ In addition, C₃S was detected in the circumstellar shell of the evolved carbon star IRC+10216.⁷⁹

The most extensive theoretical investigation of linear C₃S available in the literature was published in 1994 and was carried out by the author and his coworkers.⁸⁰ A short time later, rotational spectra of C₃S in the excited bending vibrational states $\nu_5 = 1-4$ and $\nu_4 = 1$ were published by Tang and Saito.⁸¹ In addition, the ν_1 fundamental and the accompanying hot band $\nu_1 + \nu_5 - \nu_5$ were observed by means of infrared diode laser spectroscopy.⁸² The spectroscopic properties derived from these experiments turned out to be in very good agreement with the earlier predictions.

In the present work, CCSD(T) calculations with the cc-pVQZ basis (valence electrons correlated) have been carried out. Comparison with available experimental data is made in Table 10. Throughout, agreement between experiment and theory must be considered to be very good. Remarkably, this holds even for the tiny rovibrational constants q_4^f and q_5^f . Making use of experimental values for the ground-state rotational constants of four different isotopomers and the differences $B_e - B_0$ calculated by CCSD(T)/cc-pVQZ, an improved equilibrium structure is established for C₃S: $R_{1e}(C_{(1)}C_{(2)}) = 1.2810$ Å, $R_{2e}(C_{(2)}C_{(3)}) = 1.2927$ Å and $R_{3e}(C_{(3)}S) = 1.5374$ Å. Again, these geometrical parameters are characteristic of a hetero-cumulenic system. The ratio $B_0(\text{exp.})/B_e(\text{mixed})$ is 1.00085 and thus very close to unity.

The first measurement of the electric dipole moment of C₃S was published by Lovas *et al.*⁸³ They arrived at $\mu_0 = 2.81(7)$ D and mentioned that, due to a limited frequency range in their Stark effect measurements and possible ionic shielding, this value should be considered a lower limit. Indeed, subsequent CCSD(T) calculations by the author and his coworkers yielded a considerably higher value of $\mu_e = 3.89$ D.⁸⁰ In a refined measurement, the ground-state electric dipole moment was determined to be $\mu_0 = 3.704(9)$ D.⁸⁴ A difference $\mu_e - \mu_0$ of 0.2 D appears to be quite reasonable for such a molecule; in particular, zero-point vibrational contributions from the bending modes are expected to slightly reduce the dipole moment. Core-valence and core-core electron correlation effects, which were not included in the previous CCSD(T) calculations, may also make a minor contribution to the electric dipole moment.

The first observation of the microwave spectrum of C₅S was reported in 1993 by Kasai *et al.* who detected eight rotational transitions of the most abundant species and three transitions of C₅³⁴S in the 5–20 GHz region.⁸⁵ A very tentative detection of the $J = 13-12$ transition of C₅S in the envelope of IRC+10216 was published by Bell *et al.*⁸⁶ If this assignment

is correct, the abundance of C₅S in this astronomical source would be smaller than that of C₃S by only a factor of 2.5.

Applying corrections of -0.0037 Å (cc) and -0.0071 Å (cs) to the CCSD(T)/cc-pVQZ equilibrium bond lengths for linear C₅S, which were taken over from C₃S, the following equilibrium structure is obtained for this potential interstellar molecule: $R_{1e}(C_{(1)}C_{(2)}) = 1.2838$ Å, $R_{2e}(C_{(2)}C_{(3)}) = 1.2926$ Å, $R_{3e}(C_{(3)}C_{(4)}) = 1.2662$ Å, $R_{4e}(C_{(4)}C_{(5)}) = 1.2815$ Å and $R_{5e}(C_{(5)}S) = 1.5448$ Å. This structure represents a slight improvement over the author's previous equilibrium structure as cited in ref. 80. The equilibrium rotational constant obtained here is $B_e = 922.15$ MHz, to be compared with the experimental ground-state value of $B_0 = 922.7033(2)$ MHz.⁸⁷ Again, B_0 is larger than B_e by less than 0.1%.

At the recommended equilibrium structure from this work, the dipole moment of C₅S was calculated by CCSD(T) with the aug-cc-pVQZ basis set. The result is $\mu_e = 5.320$ D. Thereof, electron correlation accounts for 1.025 D. Considering the above discussion for C₃S, the experimental ground-state value μ_0 may well be smaller than the CCSD(T) value for μ_e by about 0.2 D.

5. Pure carbon chains

5.1. Linear C₅ (X ¹Σ_g⁺)

The first high-resolution spectrum of the carbon cluster C₅ was obtained in 1989 by means of infrared astronomy. Bernath *et al.*²⁷ were able to observe 16 rovibrational lines within the ν_3 band of linear C₅ in the circumstellar envelope of IRC+10216. This band corresponds to the intense anti-symmetric CC stretching vibration with highest wavenumber. Shortly afterwards, two other groups investigated the same band in the laboratory.^{88–90} The second paper by Moazzen-Ahmadi *et al.*⁹⁰ is of particular interest, as it includes the largest number of lines in the fundamental and also reports the detection and analysis of three adjacent hot bands. The upper rovibrational states within the ν_3 band were found to be weakly perturbed by another vibrational state, for which no assignment could be given. While the ν_3 bands for all nineteen ¹³C substituted isotopomers could be observed by matrix isolation IR spectroscopy,⁹¹ only fully substituted ¹³C₅ could be investigated in the gas phase.⁹² In addition to 53 lines within the ν_3 fundamental, 66 lines within the hot band arising from the lowest bending vibrational level, $\nu_7 = 1$, were detected.

In the present work, the complete cubic force field of linear C₅ was calculated by CCSD(T) with the cc-pVQZ basis (275 cGTOs). Therefrom, spectroscopic constants were calculated which are listed in Table 11 for the most abundant species and three of its isotopomers. The calculated harmonic vibrational wavenumbers are expected to be accurate to *ca.* 5 cm⁻¹. An approximate experimental value is available for ω_3 of the most abundant species. It was derived from the experimental ν_3 values for C₅ and ¹³C₅ by making use of isotopic scaling relationships and it differs from the present CCSD(T) value by 6.8 cm⁻¹ or 0.3%. Excellent agreement between theory and experiment is observed for the five vibration-rotation coupling constants α_r for which comparison is possible. Throughout, the theoretical values are within 3% of the experimental data. As is usually observed, the calculated *l*-type doubling constants q_l are slight underestimates.

The equilibrium quartic centrifugal distortion constant of C₅, termed D_e^j , is calculated to be 119 Hz. The corresponding experimental ground-state value is 161(13) Hz, where the value in parentheses corresponds to the standard deviation (1σ). The ratio $D_0^j(\text{exp.})/D_e^j(\text{theor.})$ of 1.35 is larger than the corresponding value of 1.25 as obtained for valence-isoelectronic SiC₄,⁶⁹ but, owing to the uncertainty in the experimental D_0^j value, this is not too meaningful.

Table 10 Comparison of experimental and theoretical rovibrational constants for C₃S

| Spectroscopic constant | Exp. ^a | Theor. ^b |
|------------------------|-------------------|---------------------|
| α_1 /MHz | 14.83 | 14.41 |
| α_4 /MHz | -5.65 | -5.40 |
| q_4 /MHz | 1.51 | 1.48 |
| q_4^f /Hz | -0.48 | -0.57 |
| α_5 /MHz | -12.36 | -11.89 |
| q_5 /MHz | 3.96 | 3.82 |
| q_5^f /Hz | -11.4 | -10.5 |

^a Refs. 81 and 82. ^b CCSD(T)/cc-pVQZ. Further spectroscopic constants are available from the author upon request.

Table 11 Harmonic vibrational wavenumbers, vibration–rotation coupling constants, *l*-type doubling constants and quartic centrifugal distortion constants for four different isotopomers of linear C₅^a

| | C ₅ ^b | ¹³ CCCC | C ¹³ CCCC | ¹³ C ₅ ^b |
|---------------------------|-----------------------------|--------------------|----------------------|---|
| ω_1/cm^{-1} | 1988.7 | 1979.0 | 1957.3 | 1910.4 |
| ω_2/cm^{-1} | 778.2 | 766.5 | 774.1 | 747.6 |
| ω_3/cm^{-1} | 2221.4 (2214.6) | 2218.8 | 2202.0 | 2133.9 |
| ω_4/cm^{-1} | 1454.0 | 1438.7 | 1451.2 | 1396.8 |
| ω_5/cm^{-1} | 210.3 | 209.5 | 207.0 | 202.0 |
| ω_6/cm^{-1} | 544.1 | 544.1 | 540.1 | 522.7 |
| ω_7/cm^{-1} | 112.5 | 111.2 | 112.0 | 108.1 |
| α_1/MHz | 9.209 | 8.935 | 8.948 | 8.164 |
| α_2/MHz | 2.683 | 2.549 | 2.660 | 2.379 |
| α_3/MHz | 12.779 (12.59) | 12.357 | 12.594 | 11.329 (11.07) |
| α_4/MHz | 6.177 | 5.943 | 6.070 | 5.476 |
| α_5/MHz | -9.939 (-10.24) | -9.639 | -9.647 | -8.811 |
| α_6/MHz | -4.246 | -4.101 | -4.190 | -3.764 |
| α_7/MHz | -9.383 (-9.30) | -9.082 | -9.172 | -8.318 (-8.14) |
| ΔB_0 | -8.143 | -7.929 | -7.872 | -7.219 |
| q_5/MHz | 2.134 (2.36) | 2.008 | 2.133 | 1.892 |
| q_6/MHz | 1.008 | 0.944 | 0.999 | 0.893 |
| q_7/MHz | 3.900 (3.99) | 3.698 | 3.854 | 3.457 (3.49) |
| q_5^l/Hz | -3.462 | -3.167 | -3.416 | -2.832 |
| q_6^l/Hz | -0.254 | -0.230 | -0.249 | -0.208 |
| q_7^l/Hz | -11.157 | -10.351 | -10.836 | -9.128 |
| D_c^l/Hz | 119 (161) ^c | 112 | 118 | 102 (138) ^c |

^a CCSD(T)/cc-pVQZ (valence electrons correlated). Vibrations 1–2 of C₅ and ¹³C₅ are totally symmetric (σ_g), 3–4 belong to symmetry σ_u , 5 belongs to π_g and 6–7 belong to π_u . Since ¹³C substitution produces only small changes of the normal vibrations, the same numbering is adopted for the two asymmetrically substituted isotopomers. Spectroscopic constants for further isotopomers are available from the author upon request. ^b Experimental values (refs. 90 and 92) in parentheses. The experimental ω_3 value for C₅ is approximate (see the text). ^c Ground-state values (refs. 89 and 91).

From the theoretical α_r values, the difference between ground-state and equilibrium rotational constant of C₅ is calculated to be 8.143 MHz. It agrees well with an approximate experimental value of 8.9 MHz, obtained from experimental values for $B_0(\text{C}_5)$ and $B_0(^{13}\text{C}_5)$ through appropriate isotopic scaling considerations.⁹² Making use of the present difference and the experimental $B_0(\text{C}_5)$ we arrive at $B_c(\text{C}_5) = 2549.49$ MHz. Under the assumption that the CCSD(T)/cc-pVQZ values for the equilibrium bond lengths of linear C₅ have errors of comparable size, the above B_c value is employed to deduce a mean correction parameter of $\Delta R_c(\text{C}=\text{C}) = -0.0036$ Å. It is practically identical with the mean correction parameter of -0.0037 Å derived by comparison of CCSD(T)/cc-pVQZ results with a mixed experimental/theoretical equilibrium structure for linear SiC₄.⁶⁹

A comparison of high-quality equilibrium structures for linear C₅ is made in Fig. 8 where the results from this work are given in the last two lines. Agreement with the author's previous recommended equilibrium structure⁹⁴ is perfect for the inner CC equilibrium bond length while the present outer CC equilibrium bond length may be too large by *ca.* 0.0002 Å. The author's most recent recommended equilibrium structure is given in the last line of the figure. Needless to say, all equilibrium structures given in Fig. 8 are of higher quality than those available for most other stable penta-atomic molecules.

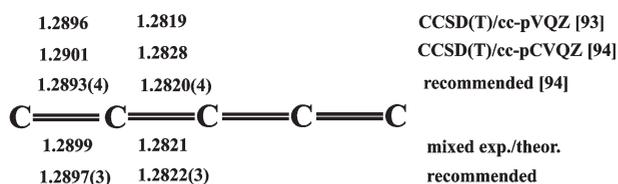


Fig. 8 Equilibrium structures for linear C₅.

5.2. Linear C₇ (X ¹Σ_g⁺)-a suitable candidate for far-infrared astronomy?

Beyond C₅, C₇ is the next closed-shell carbon cluster which is expected to be observable in the ISM. Although high-resolution spectroscopic studies of the strong ν_4 and ν_5 bands of linear C₇ (antisymmetric stretching vibrations) have been available for some time,^{95–97} no detection of this species by means of mid-IR astronomy has yet been reported. An alternative might be satellite-based spectroscopic investigation in the far IR region of the spectrum. Such an experiment appears to be quite promising, provided that linear C₇ were a flexible species exhibiting a large-amplitude bending vibration with a low wavenumber and a large transition dipole moment. According to the interpretation of their diode laser IR spectra, Saykally and coworkers concluded that linear C₇ is indeed an extremely nonrigid species with large-amplitude motion unprecedented in strongly bound molecular systems.^{96,98,99} However, recent theoretical work by the author employing CCSD(T) with the cc-pVQZ basis set came to a different conclusion.¹⁰⁰ These calculations indicated that linear C₇ is a fairly normal semirigid molecule with no sign of floppiness. In particular, excitation of the bending vibration with the lowest wavenumber (ν_{11}) was calculated to change the rotational constant by only 0.2%, far off from the 9.3% deduced by Heath and Saykally⁹⁶ from their analysis of several weaker lines accompanying the strong lines within the ν_4 band. The author's previous calculations of a near-equilibrium potential energy surface gave also no indication that, in contrast to C₃,¹⁰¹ the lowest bending vibration of C₇ should be very anharmonic. Therefore, the calculated harmonic wavenumber of $\omega_{11} = 70$ cm⁻¹ should provide a reasonably good approximation to the unknown experimental anharmonic wavenumber.

In this work, the IR intensities of the π_u bending vibrations are considered. For this purpose, the variation of the electric dipole moment with respect to the symmetry coordinates S_9 – S_{11} has been studied. These are defined as

$$S_9 = \frac{1}{\sqrt{2}}(\Delta\alpha + \Delta\alpha')$$

$$S_{10} = \frac{1}{\sqrt{2}}(\Delta\beta + \Delta\beta')$$

and

$$S_{11} = \Delta\gamma.$$

Here, α and α' are the outermost, β and β' the middle and γ is the innermost CCC bending angle. The difference coordinates $\Delta\alpha$ and $\Delta\alpha'$ or $\Delta\beta$ and $\Delta\beta'$ are defined to have the same sign for a *cis*-like distortion of the nuclear framework.

Using CCSD(T) with the aug-cc-pVQZ basis exclusive of *g* functions (434 contracted Gaussian type orbitals), the first derivatives of the perpendicular component of the electric dipole moment with respect to the above three symmetry coordinates were obtained as follows (all in atomic units):

$$\left(\frac{\partial\mu_{\perp}}{\partial S_9}\right) = -0.861, \quad \left(\frac{\partial\mu_{\perp}}{\partial S_{10}}\right) = -1.461 \quad \text{and}$$

$$\left(\frac{\partial\mu_{\perp}}{\partial S_{11}}\right) = -0.903.$$

These three derivatives were employed to calculate the absolute IR intensities of the π_u bending vibrations within the familiar double harmonic approximation, making use of the CCSD(T)/cc-pVQZ quadratic force constants reported earlier.¹⁰⁰ The results are (in km mol⁻¹):

$$A_9 = 9.2, \quad A_{10} = 10.8 \quad \text{and} \quad A_{11} = 20.7.$$

Accordingly, the intensities of the lowest bending vibrations are relatively low. This indicates that the prospects of

observing lines of linear C₇ within its ν_{11} band through far-IR spectroscopy must be considered to be rather poor.

6. Conclusions

Many of the more than 130 different molecular species which have so far been detected in the interstellar medium are highly reactive and therefore difficult to investigate in the laboratory. In particular in those cases, present day theoretical chemistry may be of great help with the identification and characterisation. High-level *ab initio* calculations for small molecules are already of such high accuracy that, for a number of spectroscopic properties, they can compete with data derived by high resolution spectroscopic studies. Quite often, they also provide important complementary information and a combination of theoretical and experimental data provides a convenient means to increase our knowledge on spectroscopic properties of interstellar molecules at a quantitative level. An example of this sort consists in the determination of accurate equilibrium structures. Following earlier work by the author and his coworkers on the smaller cyanopolyynes,^{28–31} the present paper reports an accurate equilibrium structure for HC₁₁N, the largest molecule which has been detected by radio astronomy. Abundancies of interstellar molecules are of special interest. Their determination through radio astronomical measurements requires the knowledge of electric dipole moments. For reactive species these are difficult to obtain by experiment and so theory can make a valuable contribution. The accuracy need not be particularly high; uncertainties of a few per cent are usually tolerable. In most cases it therefore suffices to calculate equilibrium dipole moments instead of dipole moments in the ground vibrational state.

Primarily in star-forming regions, a number of interstellar molecules has been detected in excited vibrational states. Compared to the ground state, such states are characterised through rovibrational constants like vibration–rotation and *l*-type doubling constants. With state-of-the-art *ab initio* calculations, such constants may be calculated to an accuracy of a few per cent which is often competitive with spectroscopic measurement. Theoretical information is particularly useful in the analysis of perturbations which frequently occur in polyatomic molecules. For example, results of coupled cluster calculations provided by the present author are currently being used in a refined spectroscopic analysis of the interstellar molecule HC₃N and its isotopomers.¹⁰²

Another important issue concerning interstellar molecules is the existence of isomers and their relative abundancies. Two isomers of cyanoacetylene could so far be detected in the ISM—linear HCCNC and quasilinear HNC₃. Some spectroscopic evidence for a third high-energy isomer (HCNCC) was published very recently.⁵⁵ In all cases, quantum-chemical calculations played a major role in making predictions for spectroscopic properties and energetics.

Over the past few years, satellite-based IR astronomy has been making progress and important organic molecules like diacetylene, triacetylene and benzene could be detected in CRL 618, a proto-planetary nebula with a thick molecular envelope.² Mid IR and far IR astronomy might also provide a means to observe pure carbon clusters larger than C₅. According to the present work, the chances of observing linear C₇ in the far IR must be considered to be poor. Extensive theoretical work on larger carbon chains up to C₁₃ is in progress¹⁰³ but again the prospects for potential astronomical detection in the far IR are not promising.

Not addressed in this article has been the nature of the carriers of diffuse interstellar bands which is a topic of its own and still a field of wide speculation (see, e.g., ref. 104) In any case, for the near future one may safely expect a continuation of the fruitful interplay between theoretical chemistry, labora-

tory spectroscopy and astronomical investigations in different spectral regions.

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