High-level ab initio quartic force fields and spectroscopic characterization of $\text{C}_2\text{N}^\text{−}$

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While it is now well established that large carbon chain species and radiative electron attachment (REA) are key ingredients triggering interstellar anion chemistry, the role played by smaller molecular anions, for which REA appears to be an unlikely formation pathway, is as yet elusive. Advancing this research undoubtedly requires the knowledge (and modeling) of their astronomical abundances which, for the case of $\text{C}_2\text{N}^\text{−}$, is largely hindered by a lack of accurate spectroscopic signatures. In this work, we provide such data for both ground $\ell$-$\text{CCN}^\text{−}(3\Sigma^\text{−})$ and low-lying $\ell$-$\text{CNC}^\text{−}(1\text{A}_1)$ isomers and their singly-substituted isotopologues by means of state-of-the-art rovibrational quantum chemical techniques. Their quartic force fields are herein calibrated using a high-level composite energy scheme that accounts for extrapolations to both one-particle and (approximate) $\ell$-particle basis set limits, in addition to relativistic effects, with the final forms being subsequently subject to nuclear motion calculations. Besides standard spectroscopic attributes, the full set of computed properties includes fine and hyperfine interaction constants and can be readily introduced as guesses in conventional experimental data reduction analyses through effective Hamiltonians. On the basis of benchmark calculations performed anew for a minimal test set of prototypical triatomics and limited (low-resolution) experimental data for $\ell$-$\text{CCN}^\text{−}(3\Sigma^\text{−})$, the target accuracies are determined to be better than 0.1% of experiment for rotational constants and 0.3% for vibrational fundamentals. Apart from laboratory investigations, the results here presented are expected to also prompt future astronomical surveys on $\text{C}_2\text{N}^\text{−}$. To this end and using the theoretically-predicted spectroscopic constants, the rotational spectra of both $\ell$-$\text{CCN}^\text{−}(3\Sigma^\text{−})$ and $\ell$-$\text{CNC}^\text{−}(1\text{A}_1)$ are derived and their likely detectability in the interstellar medium is further explored in connection with working frequency ranges of powerful astronomical facilities. Our best theoretical estimate places $\ell$-$\text{CNC}^\text{−}(1\text{A}_1)$ at about 15.3 kcal mol$^{-1}$ above the ground-state $\ell$-$\text{CCN}^\text{−}(3\Sigma^\text{−})$ species.

1 Introduction

The plausible existence and role of negative molecular ions in the interstellar medium (ISM) were put forward in the early days of astrochemistry by several authors$^{[1–3]}$. However, while their parent cation and neutral species have soon emerged as tempting targets for radioastronomical surveys$^{[4]}$ and paved the way for explaining chemical synthesis in the ISM$^{[5–9]}$, the detection of anions remained largely elusive, particularly because of a lack of accurate rest frequencies$^{[10]}$. This situation has changed recently with the laboratory and astronomical identification of the first interstellar molecular anion$^{[11]}$ $\text{C}_6\text{H}^\text{−}$. This led to a resurgence of interest of chemists, physicists, and astrophysicists in anions, motivating new surveys as well as theoretical and laboratory studies$^{[12–15]}$. As a result, several other negatively charged species were soon identified like $\text{C}_4\text{H}^\text{−}$, $\text{C}_5\text{H}^\text{−}$, $\text{C}_7\text{N}^\text{−}$, $\text{C}_8\text{N}^\text{−}$ and $\text{CN}^\text{−}$ (Refs $^{[15]}$ and references therein).

Very early on, it has been suggested$^{[21]}$ that, under typical interstellar conditions, the formation of such anionic inventory ($X^\text{−}$) could be mainly ascribed to radiative electron attachment (REA) to the existing neutrals ($X$)$^{[17,22]}$

$$X + e^− \xrightleftharpoons[k_d]{k_c} [X^\text{−}]^* \xrightarrow{k_3} X^− + h\nu.$$  \hspace{1cm} (1)

As noted elsewhere$^{[21,17,22]}$, reaction (1) implies a competition, following electron capture ($k_c$), between auto-detachment ($k_d$) and radiative stabilization ($k_3$) of the initially formed (transient) supereexcited complex $[X^\text{−}]^*$ in dilute astrophysical media, collisional stabilization of $[X^\text{−}]^*$ is assumed negligible$^{[15]}$. Using phase-space theory (PST) and relying on the mechanism (1), Herbst$^{[1]}$ first derived a theoretical expression for the overall REA rate constant ($k_{\text{REA}}$) – the results pointed towards an interesting conclusion: $k_{\text{REA}}$ increases greatly with increasing molecular size and

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electron affinity of the target neutrals. Moreover, for \( X \) species with large dipole moments (\( \mu \geq 2.5 \text{ D} \)), it has later been recognized \(^{22,24,25}\) that the existence of dipole-driven resonance and (excited) dipole-bound states are key to enhance further the \( |X^-| \)'s lifetime (with respect to auto-detachment), and hence the efficiency of REA. Thus, provided that the \( k \)'s are high, such anions can form with sizeable rates (\( k_{\text{REA}} \approx 10^{-7} \text{ cm}^3 \text{s}^{-1} \)) and, depending on the local ISM gas pressure and radiation field, exhibit appreciable anion-to-neutral ratios. \(^{22,23}\) It was for this reason that carbon chain anions were also considered possible carriers of diffuse interstellar bands. \(^{25}\)

Assuming reaction \(^1\) as the major anion formation route and using the theoretically-derived PST rates, \(^{31,18,19,22}\) previous anion chemical models have been successful in reproducing the observed abundances of the larger, highly-dipolar carbon-chain anions \( \text{C}_n\text{H}^- (n > 5) \) and \( \text{C}_n\text{N}^- (n > 4) \) in a variety of astronomical environments. \(^{15,20,21,23}\) For example, Walsh et al. \(^{23}\) determined anion-to-neutral ratios of \( \sim 4\% \), \( \sim 5\% \) and \( \sim 7\% \) for \( \text{C}_4\text{H}^- \), \( \text{C}_5\text{H}^- \) and \( \text{C}_5\text{N}^- \), respectively, values that compare quite well with the ones observed in the dark cloud TMC-1 (\( \sim 5\% \), \( \sim 2\% \) and \( \sim 13\% \)). \(^{15,19}\) These results provide further evidence in support of the REA hypothesis for such molecules. However, for the smallest anionic species (e.g., \( \text{CN}^- \) and \( \text{C}_2\text{N}^- \)) for which REA to their parent neutrals are theorized to be very slow (\( k_{\text{REA}} \approx 10^{-10} \text{ cm}^3 \text{s}^{-1} \)), notable discrepancies have soon appeared between the modeled and observed anion-to-neutral ratios \(^{15}\) suggesting that other alternative pathways might dominate their synthesis. \(^{18,25,26}\) For example, the unusually high \( \text{CN}^- \) abundance observed towards the carbon-rich star IRC+10216 has been explained \(^{21}\) by means of the reaction fragments \( \text{CN}^- + \text{N} \rightarrow \text{CN}^- + \text{C}_n\text{N}^- \), \(^{25}\) a similar synthetic route (\( \text{C}_n\text{N}^- \rightarrow \text{C}_n\text{N}^- \rightarrow \text{C}_n\text{N}^- \)) has been later proposed to also dominate the production of \( \text{C}_n\text{N}^- \) in TMC-1. \(^{15}\) Subsequent quantum mechanical calculations by Gianturco et al. \(^{29}\) provided compelling evidence in favor of the \( \text{H}^+ \text{HCN} \) reactions as additional prime sources of elemental \( \text{C}_n\text{N}^- \)'s under typical ISM conditions.

Based on laboratory experiments, Chacko et al. \(^{35}\) recently suggested a novel formation pathway for smaller interstellar \( \text{C}_n\text{N}^- / \text{C}_n^- \) species – it involves the fragmentation decay of supernovae resonance anion states of larger analogues (e.g., \( \text{[C}_n\text{N}^-]^+ \) with \( n = 3, 5, 6, 7 \)) that can be formed from impinging UV photons onto the external layers of IRC+10216 (see Eq. \(^1\)). The results pointed out the dominance of \( \text{C}_3^- \) and \( \text{C}_2\text{N}^- \) as fragmentation products, thereby offering invaluable prospects into their omnipresence in the circumstellar shells of IRC+10216. \(^{35}\) Indeed, these species are yet to be identified in space and their laboratory and theoretical characterization is tempting/timey. It should be noted that, apart from circumstellar envelopes, the conclusions drawn by Chacko et al. \(^{35}\) are expected to also prompt future astronomical surveys on \( \text{C}_3^- \) and \( \text{C}_2\text{N}^- \) in strongly shielded environments like TMC-1, although their existence therein (if at all) must entail distinct chemical formation routes. Thus, studying the astronomical abundance of these smaller species is key to a proper understanding of a ISM anion chemistry beyond REA. \(^{31}\) For this, accurate spectral features of such molecules should then be gathered. Still, while \( \text{C}_3^- \) is spectroscopically well-characterized in the laboratory (Ref. \(^{37}\) and references therein), the amount of theoretical and experimental data on the carbonitrile anion \( \text{C}_2\text{N}^- \) is as yet very limited. \(^{39,41}\)

In light of the foregoing, this work thus aims at providing accurate rovibrational spectroscopic constants and anharmonic vibrational frequencies for \( \text{C}_2\text{N}^- \) by means of a high-level theoretical approach (see below). Indeed, its parent neutral form, \( \ell \)-\( \text{CCN}^-(\Pi) \), has only recently been detected in the circumstellar envelope of IRC+10216. \(^{32}\) Despite having a relatively small dipole moment (\( \mu \approx 0.3 \text{ D} \)), \( \ell \)-\( \text{CCN}^-(\Pi) \) is characterized by a high (positive) electron affinity, \( \text{EA} = 2.7489 \pm 0.0001 \text{ eV} \), hence rendering the corresponding ground-state anion, \( \ell \)-\( \text{CCN}^-(\Sigma^-) \), exceptionally stable with respect to electron loss. \(^{35,39}\) See Figure 1

As in the case of \( \text{C}_3^- \), this is manifested in the very existence of bound electronically excited \( \text{C}_2\text{N}^- \) states that lie below its photodetachment threshold (Figure 1) and that can be optically connected to \( \ell \)-\( \text{CCN}^-(\Sigma^-) \). Such a high electron binding energy, in combination with a large dipole moment (\( \mu \approx 2.0 \text{ D} \)), makes \( \ell \)-\( \text{CCN}^-(\Sigma^-) \) amenable to observation with new powerful instruments such as the atacama large millimeter/submillimeter array (ALMA) and the Green Bank Telescope (GBT). Apart from the linear ground-state, a low-energy cyclic \( \text{C}_2 \) form of \( \text{C}_2\text{N}^- \), \( \ell \)-\( \text{CNC}^-(\Lambda_1) \), lying ca. 15kcalmol\(^{-1}\) above \( \ell \)-\( \text{CCN}^-(\Sigma^-) \) exists (Figure 1) that may be equally relevant to interstellar chemistry. \(^{39,44}\) and is likewise focus of the present study. Indeed, besides acyclic (small) cyano precursors, \(^{35,45}\) there is compelling evidence that such elemental N-heterocycles might also play a role into the chemical evolution of larger astrobiologically-relevant species. \(^{37}\) In addition to interstellar and circumstellar environments, we should also mention the likely pertinence of these nitrile anions to the atmosphere of Titan wherein a rich N-based anion chemistry is known to prevail. \(^{48}\)

As for their theoretical spectroscopic characterization, we
herein employ the so-called quartic force field (QFF) approach. Within this framework, the potential energy surfaces (PESs) of \( \text{C-CN}^{-1}\) and \( \text{C-CNC}^{-1} \) are represented locally by fourth-order Taylor series expansions:

\[
V(R) = \frac{1}{2} \sum_{\gamma} F_{ij} \Delta_i \Delta_j + \frac{1}{6} \sum_{ijk} F_{ijk} \Delta_i \Delta_j \Delta_k + \frac{1}{24} \sum_{ijkl} F_{ijkl} \Delta_i \Delta_j \Delta_k \Delta_l, \tag{2}
\]

where \( R = \{R_1, R_2, R_3\} \) denotes an arbitrary set of internal coordinates, \( \Delta_i = R_i - R_i^0 \) represent coordinate displacements from the equilibrium geometries \( \mathbf{R}_e = \{R_1^0, R_2^0, R_3^0\} \) and \( F_{ij} = \ldots = \frac{\partial^2 V}{\partial \Delta_i \partial \Delta_j \ldots} |_{\Delta_i = 0} \) the force constants; the unrestricted summations run over all possible coordinate indices \( 3 \geq i, j, k, l \geq 1 \). These QFFs will then be computed using highly accurate ab initio energies, with the final forms being subsequently subject to nuclear motion calculations. The details of such a methodology are scrutinized in section 2 while the results are presented in Section 3. The astrophysical implications are briefly surveyed in Section 4 with the conclusions being gathered in Section 5.

2 Theoretical methods

2.1 Ab initio calculations & QFFs

The full QFFs for the C\(_2\)N anions were computed by performing accurate ab initio calculations on equally spaced grid points centered at best-guess equilibrium structures (see below). A total of 85 symmetry-unique geometries were sampled based on a finite (central) difference approach; the step lengths taken were \( \pm 0.005 \) Å/rad. In generating such grids for \( \text{C-CN}^{-1}\) \( \text{C-CNC}^{-1} \), we have employed simple internal displacement coordinates, i.e.,

\[
\Delta_1 = r(C_1 - N) - r_e(C - N),
\]

\[
\Delta_2 = r(C_1 - C_2) - r_e(C - C) \quad \text{(3)}
\]

for stretches and

\[
\Delta_{3,4} = \sin(\angle(C - C - N)) - \sin(\angle_e(C - C - N)) \quad \text{(4)}
\]

for the degenerate linear bends; \( r \) and \( \angle \) define bond lengths and angle, respectively, with the subscript \( e \) denoting the corresponding equilibrium values; see Figure 2. Note that only one component, \( \Delta_4 \), was considered in the finite difference calculations; bending force constants depending on \( \Delta_4 \) are herein determined via cylindrical symmetry relations.

\[
F_{3344} = (F_{333} + 4F_{333})/3, \quad F_{333} = F_{344},
\]

\[
F_{33i} = F_{44i}, \quad F_{33} = F_{44} \quad \forall i, j. \quad \text{(5)}
\]

For \( \text{C-CN}^{-1}(1\text{\,A}_1) \), the following symmetry-internal displacement coordinates were used:

\[
\Delta_1 = \frac{1}{\sqrt{2}} [r(N - C_1) + r(N - C_2) - 2r_e(N - C)]
\]

\[
\Delta_2 = \angle(C - N - C) - \angle_e(C - N - C)
\]

\[
\Delta_3 = \frac{1}{\sqrt{2}} [r(N - C_1) - r(N - C_2)]. \quad \text{(6)}
\]

At each selected geometry \( R \), the total electronic energy, \( E \), was then obtained via a composite scheme:

\[
E(R) = E_{CC}^\infty (R) + \Delta_{\text{DKH}}(R) + \Delta_{\text{HO}}(R), \quad \text{(7)}
\]

where \( E_{CC}^\infty \) is an estimate of the one-particle complete basis set (CBS) limit, including core and core-valence correlation, at the coupled cluster singles and doubles level of theory with perturbative triple \( \text{(CCSD(T) or, briefly, CC)} \), \( \Delta_{\text{DKH}} \) is a correction for scalar relativistic effects, and \( \Delta_{\text{HO}} \) accounts for higher-order (HO) electron correlation contributions beyond CC. All calculations have been performed at the spin-restricted (open-shell) CC level of theory using the restricted (open-shell) Hartree-Fock (HF) determinant as reference. The VXX (\( X = D.T.Q, 5 \)) basis sets of Dunning and co-workers \( \text{[57]} \) with additional diffuse \( \text{AVXZ} \) and core correlation functions \( \text{[59]} \) (ACVXZ) were employed throughout, with the computations done with MOLEPS. To ensure accuracy of the final force constants, all calculations have been carried out with a convergence energy criteria of \( 10^{-12} \ h_\text{a} \) \( \text{[51-53]} \).

Due to the distinct asymptotic convergence rates, the CBS extrapolations for the HF and total CC electron correlation (cor) components of \( E_{CC}^\infty \) (Eq. (7)) were performed individually, i.e.,

\[
E_{CC}^\infty (R) = E_{\text{HF}}(R) + E_{\text{cor}}^\infty (R). \quad \text{(8)}
\]

For the HF energy, a three-point exponential-type formula has been so employed:

\[
E_{X}^{\text{HF}}(R) = E_{\text{HF}}(R) + A \exp(-BRX), \quad \text{(9)}
\]

where \( E_{\text{HF}}, A, \) and \( B \) are parameters to be calibrated from HF/ACVXZ (\( X = T, Q, 5 \)) energies. In turn, the extrapolated cor contributions are obtained via the inverse-power formula:

\[
E_{X}^{\text{cor}}(R) = E_{\text{cor}}^\infty (R) + A'X^{-3} + B'X^{-5}, \quad \text{(10)}
\]

where \( E_{\text{cor}}, A', \) and \( B' \) are calibrated from the raw CC/ACVXZ (\( X = T, Q, 5 \)) total correlation energies.

In Eq. (7), the corrections due to scalar relativistic contributions were obtained by

\[
\Delta_{\text{DKH}}(R) = E_{\text{DKH}}(R) - E_{\text{NR}}(R), \quad \text{(11)}
\]

where \( E_{\text{DKH}} \) is the total second-order Douglas-Kroll-Hess (DKH) \( \text{[24][27][34]} \) CC energy calculated with the VTZ-DK basis set. \( E_{\text{NR}} \) defines its non-relativistic CC/VTZ-DK counterpart. As for the estimation of higher-order electron correlation, \( \Delta_{\text{HO}} \) (Eq. (7)), we herein include three additional (frozen-core) energy incre-
\[
\Delta_{\text{HO}}(R) = \Delta T(R) + \Delta Q(R) + \Delta \text{FCI}(R),
\]
(12)

where \(\Delta T\) and \(\Delta Q\) account for the residual CC correlation components associated with iterative triple (\(T_3\)) and quadruple (\(T_4\)) excitations; the first is obtained via differences in energy between CCSDTQ and CCSD(T) calculations with the \(\text{VQZ}\) basis set, while the second is determined from CCSDTQ and CCSD(T) values. The importance of such corrections (and cost-effective variants) for accurate predictions of spectroscopic/thermochemical properties of small-to-medium sized molecules has been emphasized in several previous works.\(^{67,68}\) Furthermore, to account for the small, residual errors arising from the truncation of the \(N\)-particle expansions at the CCSD(T) level, we also include in Eq. (12) an estimate of the difference in correlation energy between CCSD(TQ) and full configuration interaction (FCI), \(\Delta\text{FCI}\), calculated with the \(\text{VDZ}\) basis set \((X = D)\). The FCI limit was then obtained via a continued fraction (cf) approximant:\(^{69}\)

\[
E_{\text{FCI}}^X(R) \approx \frac{E_{\text{CCSD}}^X}{1 - \left(\frac{\delta_{E_{\text{CCSD}}^X}}{E_{\text{CCSD}}^X} \right) / \left(1 - \frac{\delta_{E_{\text{CCSD}}^X}}{E_{\text{CCSD}}^X} \right)},
\]
(13)

where \(\delta_{E_{\text{CCSD}}^X} = E_{\text{CCSD}}^X - E_{\text{CCSD}}^X\) and \(\delta_{E_{\text{CCSD}}^X} = E_{\text{CCSD}}^X - E_{\text{CCSD}}^X\). Thus, \(\Delta\text{FCI}\) in Eq. (12) is defined as \(E_{\text{FCI}}^X - E_{\text{CCSD}}^X\). For systems with small-to-moderate multireference character (the \(T_1\) diagnostic values for \(\ell\)-CCN\(^{−1}(3\Sigma^−)\) and \(\ell\)-CNC\(^{−1}(1\Lambda_1)\) are \(\approx 0.025\) and \(0.012\), respectively), Eq. (13) has shown to be a viable alternative for estimating electron correlation beyond CCSD(TQ), recovering nearly 80% of available FCI corrections.\(^{67,68}\) It should be noted, however, that, while the use of the CCSDTQP method\(^{88}\) and larger basis sets, e.g., \(\text{VTZ}\), would be preferable in estimating \(E_{\text{FCI}}^X\) (see, e.g., Ref. 77) and \(\Delta Q\), respectively, the associated computational cost would make the task of calculating the QFFs intractable with current available resources; all HO corrections have been computed with the \(\text{MRCI-CCSD}\) code.

Due to a lack of accurate experimental geometries for \(\text{C}_2\text{N}^−\), the determination of the reference structures in which to expand our QFFs relied solely on high-level \textit{ab initio} estimates.\(^{59}\) This has been done by first optimizing geometries at the \(\text{CC/AVTZ}\) level, followed by computations of cost-effective QFFs therein using CBS-extrapolated CC/AVXZ (\(X = D, T, Q\)) plus \(\Delta\text{KH}\) energies [Eqs. (8)-(11)]. The resulting fine-tuned minima were then utilized as reference for final geometry displacements and energy evaluations via Eq. (7). Of course, as these optimum configurations are not exact minima on the final composite PESs, accurate QFFs and equilibrium geometries could only be obtained by least-squares fitting such a composite energy set to Eq. (2); the sum of squared residuals were typically \(10^{−15}\).\(^{52}\) with the resulting force constants being numerically defined in Table 1.

### Table 1 Internal coordinate force constants for the \(\text{C}_2\text{N}^−\) anions as determined from our final composite QFFs [Eqs. (6) and (7)]. Units are \text{mdyn}\,\text{Å/}^\circ\text{m}\;\text{rad}^−\text{m}^−\text{app}r\text{ropriate for an energy unit of \text{mdyn/Å}.} \text{Eqs. (3)-(6) define the coordinates.}

| \(\ell\)-CCN\(^{−1}(3\Sigma^−)\) | \(\ell\)-CNC\(^{−1}(1\Lambda_1)\) |
|----------------|----------------|
| **QFF\(^a\)** | **QFF\(^a\)** | **QFF\(^b\)** |
| \(F_{11}\) | 12.364302 | 8.601837 | 8.613181 |
| \(F_{21}\) | 2.083929 | 3.701487 | 3.697293 |
| \(F_{22}\) | 5.491370 | 6.094652 | 6.098824 |
| \(F_{33}/44\)^\(c\) | 0.414145 | 5.415849 | 5.451568 |
| \(F_{11}\) | −94.3113 | −37.2385 | −37.1905 |
| \(F_{21}\) | 2.4761 | −11.6437 | −11.5930 |
| \(F_{22}\) | −6.9087 | −23.3909 | −23.3002 |
| \(F_{33}/44\)^\(c\) | −0.8749 | −26.7040 | −26.6360 |
| \(F_{11}\) | −38.6440 | −46.5351 | −46.2960 |
| \(F_{33}/44\)^\(c\) | −0.4844 | −2.0261 | −1.9450 |
| \(F_{111}\) | 497.67 | 133.99 | 133.55 |
| \(F_{111}\) | 21.11 | 29.28 | 29.29 |
| \(F_{221}\) | −17.79 | 54.40 | 54.25 |
| \(F_{331}/441\)^\(c\) | −0.30 | 103.14 | 102.91 |
| \(F_{331}/441\)^\(c\) | 16.36 | 119.50 | 118.99 |
| \(F_{332}/442\)^\(c\) | 2.43 | −18.96 | −18.22 |
| \(F_{332}/442\)^\(c\) | 207.87 | 316.24 | 313.96 |
| \(F_{333}/444\)^\(c\) | −0.75 | −41.59 | −40.55 |
| \(F_{334}\)^\(c\) | 2.16 | 74.07 | 73.89 |

\(^a\) This work.

\(^b\) Ref. 40.

\(^c\) Only relevant for \(\ell\)-CCN\(^−\); see Eq. 5.

2.2 (Ro)Vibrational calculations and spectroscopic constants

With such QFFs at hand, the corresponding rovibrational energy levels and associated spectroscopic constants can then be determined by solving the nuclear Schrödinger equation (NSE)\(^{54}\). This has been here accomplished through standard second-order perturbation theory (VPT2)\(^{59}\) as implemented in \texttt{SPECTRO}.\(^{60}\) As usual,\(^{40,52}\) \texttt{SPECTRO} requires the input of the appropriate resonances; for \(\ell\)-CCN\(^{−1}(3\Sigma^−)\), they correspond to Fermi type-1 (\(2\nu_5 \approx \nu_3\)), while type-C Coriolis (\(2\nu_5 \approx \nu_3\)) and Darling-Dennison (\(2\nu_5 \approx \nu_3\)) resonances are input for \(\ell\)-CNC\(^{−1}(1\Lambda_1)\). Besides VPT2, rovibrational band origins were also obtained using the exact kinetic energy nuclear motion code DVRMIN\(^{59}\) which computes variationally exact solutions to the three-atom NSE within the framework of the discrete variable representation\(^{59}\); sample \texttt{SPECTRO}
inputs and the parameters employed in DVR3D are given in the Electronic Supplementary Information (ESI). Note that, to avoid non-physical results and ensure the correct limiting behavior of the PESs, the QFFs of $\ell$-CCN$^-(\Sigma^-)$ and c-CNC$^-(\Sigma^-)$ have been analytically transformed into Morse-sine and Morse-cosine coordinate representations, respectively, prior to the variational DVR3D calculations (VAR); the reader is addressed to Refs. 90 and 91 for further details.

2.3 Benchmark calculations

To assess the performance of the above protocol, preliminary benchmark calculations have been carried out for a limited set of triatomics for which accurate gas-phase experimental data are available. The selected targets comprise the prototypical $\ell$-HCN($\Sigma^+$) and $\ell$-H$_2$O($\Sigma^+$) molecules as well as $\ell$-CCO($\Sigma^-$), an open-shell species that is isoelectronic to C$_2$N$^-$, hence expected to show a similar electronic structure; the final force constants and detailed data analysis are presented in Tables S2-S4. The results indicate that our present methodology is capable of producing vibrationally-averaged rotational constants and vibrational fundamentals to within $\sim 0.1\%$ (22 MHz) and $\sim 0.3\%$ (3 cm$^{-1}$) of experiment, respectively, for species with at least two heavy atoms, hence further showcasing its reliability. This is about the accuracy one might expect for the predicted spectroscopic attributes of $\ell$-CCN$^-(\Sigma^-)$ and c-CNC$^-(\Sigma^-)$ and is quite consistent with well-established state-of-the-art QFF/VPT2 protocols currently available in the literature [49,53,80,82].

3 Results

Figure 3 displays the dependence of the $\ell$-CCN$^-(\Sigma^-)$ and c-CNC$^-(\Sigma^-)$ harmonic frequencies for the three fundamental modes ($\omega_i$) on the ACVXZ basis set size at the CC level as well as upon inclusion of the $\Delta$DKH [Eq. (11)] and $\Delta$HO [Eq. (12)] energy increments [Eq. (7)]; the corresponding profiles obtained for equilibrium geometries ($R_i^e$) are depicted in Figure S1 (see also Figure 2 to assess their final values). Tables 2–8 gather the calculated rovibrational spectroscopic constants, vibrational fundamentals and anharmonic constants for the various C$_2$N$^-$ forms as obtained from our final composite QFFs and VPT2/VAR. Note that, apart from the main isotopologues, detailed spectroscopic data are also presented for the 13C and 15N singly-substituted species.

3.1 Effects of various corrections on equilibrium properties

A close inspection of Figure 3 unravels the slow convergence rates of the raw CC/ACVXZ ($X=T,Q,S$) harmonic frequencies towards the predicted CBS values, a feature clearly expected from standard all electron (ae) CC methods [82] see shaded gray areas and the black dashed lines outlined therein. A similar convergence behavior is also found for the $R_i^e$’s (Figure S1). In-
Table 2 Equilibrium structures and spectroscopic vibration-rotation constants of $\ell$-CCN$^-$ ($^1\Sigma^-$) isotopologues. Data determined from our final composite QFF (Table I) via second-order perturbation theory (VPT2). The bottom part gathers the ab initio calculated fine and leading hyperfine interaction constants at the QFF equilibrium geometry. Units are MHz unless stated otherwise.

|          | $\ell$-CCN$^-$ | $\ell$-$^{13}$CCN$^-$ | $\ell$-C$^{13}$CN$^-$ | $\ell$-CC$^{15}$N$^-$ |
|----------|----------------|------------------------|------------------------|------------------------|
| $r_0$(C–C)/pm | 136.1860 | 136.1765 | 136.1882 | 136.1839 |
| $r_0$(C–N)/pm | 120.6613 | 120.6565 | 120.6562 | 120.6600 |
| $\angle_0$(C–C–N)/$^\circ$ | 180.0000 | 180.0000 | 180.0000 | 180.0000 |
| $B_0$ | 11861.91 | 11369.30 | 11862.02 | 11490.06 |
| $B_1$ | 11796.21 | 11307.99 | 11800.31 | 11423.77 |
| $B_2$ | 11893.37 | 11399.60 | 11891.87 | 11520.70 |
| $B_3$ | 11795.79 | 11309.84 | 11791.59 | 11429.12 |
| $10^3D_x$ | 6.130 | 5.692 | 6.128 | 5.700 |
| $10^3H_e$ | -0.002 | -0.002 | -0.002 | -0.002 |
| $q$ | -28.489 | -26.346 | -29.257 | -26.867 |
| $\alpha_0^q$ | 65.7 | 61.3 | 61.7 | 66.3 |
| $\alpha_0^g$ | -31.5 | -30.3 | -29.8 | -30.6 |
| $\alpha_0^g$ | 80.2 | 76.3 | 80.7 | 75.2 |
| $r_0$(C–C)/pm | 135.9387 | - | - | - |
| $r_0$(C–N)/pm | 120.3706 | - | - | - |
| $\angle_0$(C–C–N)/$^\circ$ | 180.0000 | - | - | - |
| $B_e$ | 11903.44 | 11407.80 | 11903.38 | 11530.17 |
| $\mu_{e}/D$ | 1.9873 | 1.8190 | 1.9869 | 2.1347 |
| $\lambda_0^c$ | 11958.87 | - | - | - |
| $\gamma_0^c$ | -19.16 | -18.37 | -19.16 | -18.56 |
| $b_F$($^{14}$N)$^d$ | 19.84 | 19.84(65.03) | 19.84(−49.72) | - |
| $c$($^{14}$N)$^d$ | -16.24 | -16.24(−56.62) | -16.24(15.80) | - |
| $eQq$($^{14}$N)$^e$ | -2.9088 | - | - | - |
| $\eta$($^{14}$N)$^e$ | 0.0000 | - | - | - |

|          | $\ell$-CCN$^-$ | $\ell$-$^{13}$CCN$^-$ | $\ell$-C$^{13}$CN$^-$ | $\ell$-CC$^{15}$N$^-$ |
|----------|----------------|------------------------|------------------------|------------------------|

a This work. Data obtained using SPECTRE. Rotational constants ($B_i$), vibration-rotation interaction constants ($eD_{ij}$), quartic ($D_i$) and sextic ($H_i$) centrifugal distortion parameters and $\ell$-type doubling constant ($q$) are all in MHz. $B_i$ with $i=1$-3 are effective rotational constants calculated for the three vibrational fundamentals; see Figure 9 for mode descriptions. The corresponding zero-point level constant is $B_0$.

b CBS-extrapolated dipole moments (in D) at the QFF equilibrium geometry; see Ref. 22.

c Spin-spin ($\lambda_i$) and spin-rotation ($\gamma_i$) coupling constants (in MHz); see text.

d Electron spin-nuclear spin hyperfine coupling constants. Isotropic Fermi-contact ($b_F$) and anisotropic dipole-dipole ($c$) magnetic couplings (both in MHz) evaluated at the $^{14}$N nucleus. The corresponding values obtained at $^{13}$C are given in parentheses; couplings at $^{15}$N are not explicitly considered.

e CBS-extrapolated $^{14}$N nuclear quadrupole (hyperfine) coupling constant ($eQq$ in MHz) and asymmetry parameter ($\eta$) unitless; see text.

deed, on going from the smaller ACVTZ to the ACV5Z basis set, the predicted CCSD(T) equilibrium bond distances decrease by $\approx$0.01 Å, followed by increments of $\approx$0.1 Å in the corresponding harmonic frequencies. In turn, extrapolations to the CBS limit produce only minor changes in the CC/ACV5Z attributes, as expected: the $\omega_i$’s and $K_i$’s vary by less than $+2$ cm$^{-1}$ and $-0.002$ Å $/$0.005 deg, respectively. Moreover, the inclusion of scalar relativity [DKH in Eq. (11)] into $E_{\text{CC}}^c$ [Eqs. (8)–(10)] leads to only slight, but still significant reductions in both $\omega_i$ and $K_i$.

As expected for such light molecules, these corrections are small and amount to $\approx$−62 mE$_{h}$ around equilibrium. In addition to the one-particle basis set correlation recovery at CC, Figures 9 and S1 also permit an approximate assessment of the $\omega_i$ and $K_i$ convergence rates upon increasing coupled cluster $\mathcal{A}$-particle expansions [CCSD(T)$\rightarrow$CCSDT$\rightarrow$CCSDTQ$\rightarrow\approx$FCI]; see white regions and orange dashed lines. When added to the $E_{\text{CC}}^c + \Delta_{\text{DKH}}$ components, the CCSDT corrections to CCSD(T), $\Delta T$ in Eq. (12), are shown to slightly overestimate (underestimate) the bond angle (bond distances) of c-CNC$^-$ ($^1A_1$), thus leading to a net increase in the $\omega_i$’s; the contrary is the case for the linear species. Indeed, the $\Delta T$ correlation contributions to the total energies assume opposing signs for c-CNC$^-$ ($^1A_1$) and $\ell$-CCN$^-$ ($^1\Sigma^-$), being of the order of $+0.6$ and $-1$ mE$_{h}$, respectively. Yet, faster convergence rates of these equilibrium properties towards their (approximate) FCI limit values are clearly perceived after the addition of the correlation component due to iterative quadruples, $\Delta Q$ [Eq. (12)]. As noted elsewhere, the weaker dependence on the basis set size and the increasingly faster convergence rates of the HO terms (notably $\Delta T$) are demonstrably attributed to their intimate relation to non-dynamical rather than dynamical correlation. In fact, at the CCS-DTQ level, the predicted equilibrium geometries and harmonic
Table 3 Equilibrium structures, A-reduced Hamiltonian spectroscopic constants (in the \( \Pi \) representation), and vibration-rotation interaction constants of \( c \)-CNC\(^{1}(A_{1}) \) isotopologues. Data determined from our final composite QFF (Table 1) via second-order perturbation theory (VPT2)\(^{25,25} \). The top part gathers the \( ab \) initio calculated leading hyperfine interaction constants at the QFF equilibrium geometry. Units are MHz unless stated otherwise.

|          | c-CNC\(^{-}\) | c-\(^{13}\)CNC\(^{-}\) | c-C\(^{15}\)NC\(^{-}\) |
|----------|---------------|-----------------|-----------------|
|          | QFF\(^{a}\)   | QFF\(^{b}\)   | QFF\(^{a}\)   | QFF\(^{b}\)   | QFF\(^{a}\)   | QFF\(^{b}\)   |
| \( r_{0}(N–C)/\text{pm} \) | 136.3000       | 136.2734       | 136.2858       | 136.2593       | 136.2903       | 136.2637       |
| \( \angle_{D_{o}}(C–N–C)/^\circ \) | 64.800         | 64.812         | 64.796         | 64.808         | 64.804         | 64.816         |
| \( A_{0} \)       | 43384.08       | 43406.38       | 42962.76       | 42983.82       | 41567.27       | 41588.32       |
|          | 39690.76       | 39692.55       | 37968.13       | 37970.92       | 39690.61       | 39692.89       |
| \( C_{0} \)       | 20644.40       | 20650.27       | 20075.91       | 20081.47       | 20222.86       | 20228.62       |
| \( A_{1} \)       | 43112.40       | 43135.49       | 42683.37       | 42705.39       | 41323.55       | 41345.21       |
| \( B_{1} \)       | 39544.95       | 39548.05       | 37843.00       | 37846.70       | 39532.99       | 39536.49       |
| \( C_{1} \)       | 20543.71       | 20550.14       | 19980.79       | 19986.89       | 20123.93       | 20130.19       |
| \( A_{2} \)       | 43682.21       | 43702.28       | 43226.36       | 43245.79       | 41841.29       | 41860.34       |
| \( B_{2} \)       | 39316.60       | 39322.04       | 37639.10       | 37644.64       | 39309.04       | 39334.66       |
| \( C_{2} \)       | 20526.23       | 20532.55       | 19960.63       | 19966.63       | 20111.50       | 20117.66       |
| \( A_{3} \)       | 43068.78       | 43092.86       | 42682.84       | 42705.30       | 41268.88       | 41291.64       |
| \( B_{3} \)       | 39775.85       | 39778.95       | 38023.34       | 38027.50       | 39774.62       | 39777.98       |
| \( C_{3} \)       | 20512.25       | 20519.05       | 19949.32       | 19955.76       | 20093.81       | 20100.50       |
| \( 10^{3}\Delta_{J} \) | 117.187       | 117.065        | 106.299        | 106.161        | 116.772        | 116.650        |
| \( 10^{3}\Delta_{K} \) | 80.725         | 81.807         | 56.421         | 57.192         | 90.260         | 91.279         |
| \( 10^{3}\delta_{J} \) | 49.439         | 49.381         | 44.453         | 44.386         | 49.647         | 49.589         |
| \( 10^{3}\delta_{K} \) | 86.773         | 86.145         | 90.374         | 89.849         | 76.408         | 75.819         |
| \( 10^{3}\Phi_{J} \) | 0.091          | 0.101          | 0.214          | 0.219          | 0.091          | 0.101          |
| \( 10^{3}\Phi_{K} \) | 5.884          | 5.802          | 2.367          | 2.370          | 5.475          | 5.395          |
| \( 10^{3}\Phi_{J,K} \) | -23.461        | -23.196        | -12.098        | -12.081        | -21.689        | -21.439        |
| \( 10^{3}\Phi_{K} \) | 19.839         | 19.635         | 11.194         | 11.172         | 18.191         | 18.002         |
| \( 10^{3}\Phi_{K} \) | 0.044          | 0.049          | 0.106          | 0.108          | 0.044          | 0.049          |
| \( 10^{3}\Phi_{K} \) | 2.240          | 2.216          | 0.780          | 0.790          | 2.104          | 2.080          |
| \( r_{0}(N–C)/\text{pm} \) | 135.6664       | 135.6422       | -              | -              | -              | -              |
| \( \angle_{D_{r}}(C–N–C)/^\circ \) | 64.746         | 64.759         | -              | -              | -              | -              |
| \( A_{r} \)       | 43528.50       | 43550.61       | 43110.62       | 43131.31       | 41701.32       | 41722.20       |
| \( B_{r} \)       | 39908.19       | 39907.41       | 38167.60       | 38167.89       | 39908.19       | 39907.66       |
| \( C_{r} \)       | 20819.90       | 20824.75       | 20244.40       | 20249.04       | 20392.53       | 20397.38       |
| \( \mu_{e}/D_{c}^{f} \) | 1.1011         | 1.10           | 1.0536         | 1.1908         |
| \( eQ_{y}(^{14}\text{N})^{d} \) | 5.0986         | -              | -              | -              |
| \( \eta(^{14}\text{N})^{d} \) | 0.0385         | -              | -              | -              |

\(^{a}\) This work. Data obtained using SPECTR\(^{e}\). Rotational constants (\( A_{r}, B_{r}, C_{r} \)), vibration-rotation interaction constants (\( \alpha_{r}^{\Pi}, \alpha_{r}^{\Pi}, \alpha_{r}^{\Pi} \)), quartic (\( \Delta_{J}, \Delta_{K}, \delta_{J}, \delta_{K} \)) and sextic (\( \Phi_{J}, \Phi_{K}, \Phi_{J,K}, \Phi_{J}, \Phi_{J,K}, \Phi_{K} \)) centrifugal distortion parameters are all in MHz. \( A_{i}, B_{i}, C_{i} \) with \( i = 1 \)–3 are effective rotational constants calculated for the three vibrational fundamentals; see Figure\(^{f}\) for mode descriptions. The corresponding zero-point level constants are \( A_{0}, B_{0}, C_{0} \).

\(^{b}\) Ref.\(^{40} \).

\(^{c}\) CBS-extrapolated dipole moments (in D) at the QFF equilibrium geometry; see Ref.\(^{93} \).

\(^{d}\) CBS-extrapolated \(^{14}\text{N} \) nuclear quadrupole (hyperfine) coupling constant (\( eQ_{y} \) in MHz) and asymmetry parameter (\( \eta \) unitless) at the QFF equilibrium geometry; see text.
frequencies appear to be well converged for both species, with the inclusion of the ΔFCI \([Eqs. (12) \text{ and } (13)]\) terms being responsible for less than 0.0001 Å/−0.005 deg and -1 cm⁻¹ adjustments, respectively; see Figures 3 and S1. As expected, ΔQ is the largest among all HO corrections, amounting to \(\approx -0.1 \text{ mE}_h\); ΔFCI is of the order of \(\approx -0.1 \text{ mE}_h\). To gauge the reliability of our predicted ΔFCI corrections to CCSDTQ, we have followed Ref. [27] and for comparison estimated this limit at the QFF equilibrium geometry with the cc approximant \([Eqs. (13)]\) but using instead the CCSDT/VQZ, CCSDTQ/VQZ, and CCSDTQP/VQZ higher hierarchical sequence; the final CC corrections obtained in this way include additional ΔP terms and are thereafter denoted as ΔFCI_{cc}. The results have shown that our “cost-effective” cc protocol based on the CCSD→CCSDT→CCSDTQ sequence series recovers nearly 80% of the “true” residual FCI correlation energies \([i.e., \Delta \text{FCI/FCI}_{cc} \approx 0.75 \text{ and } 0.8 \text{ for } \ell-\text{CCN}^- (\Sigma^-) \text{ and } \ell-\text{CNC}^- (\Sigma^-)\), respectively], hence confirming its feasibility and accuracy. Similar conclusions were drawn in previous studies [27,28]. It should be emphasized that, although specialized extrapolation formulas have recently been developed for HO terms [29], no attempts have here been made to estimate these corrections at the CBS limit as this would imply a formidable computational effort. Thus, small additional (residual) one-particle basis set truncation errors may still be foreseen in our protocol, albeit with conceivably little impact on the final results. Of course, the magnitude of these uncertainties is expected to exceed those associated with diagonal Born-Oppenheimer (DBO) and non-adiabatic corrections [30], and we therefore opted not to include them either in our approach. Note that a high-level QFF already exists in the literature for \(\ell-\text{CCN}^- (\Sigma^-)\) [31]. It is based on the well-established CcCR protocol which includes, in addition to CBS-extrapolated CC/AVXZ \((X = T, Q, 5)\) energies, core-valence and relativistic effects [14-15,30,31,32]. For comparison, we also plot in Figures 3(b) and S1(b) the predicted CcCR equilibrium properties taken from Ref. [40]. Accordingly, the CcCR results agree quite well with our predicted attributes, notably when compared with the \(E_{\text{CC}} + \Delta_{\text{DKH}}\) PES (as expected). This provides further evidence on the reliability of our CBS extrapolation protocol \([Eqs. (8) \text{ and } (10)]\). Yet, the small discrepancies found for \(R_e^*\) and \(a_0\) \((\approx 0.0002 \text{ Å}/0.01 \text{ deg} \text{ and } \leq 4 \text{ cm}^{-1}\) are clearly attributed to the effects of HO correlations; see Tables 1, S3, and S5 and later discussions for further comparisons. Unfortunately, no experimental data is yet available for this species. This is due to the combined fact that \(\text{C}_2\text{N}^-\) molecules are not easy to produce in larger amounts and may be spectroscopically hard to identify without guiding theoretical predictions.

### 3.2 Molecular structures and rotational constants

As Table 2 shows, the computed \(\text{C}–\text{C}\) and \(\text{C}–\text{N}\) equilibrium bond distances for \(\ell-\text{CCN}^- (\Sigma^-)\) using our final composite PES are 1.359387 and 1.203706 Å, respectively. This structure is fairly close to the best-guess initial geometry \((1.359176 \text{ and } 1.201802 \text{ Å})\) utilized in the generation of the QFF \textit{ab initio} grid points \(\text{(section 2.1)}\). To the best of our knowledge, available literature data on the \(\ell-\text{CCN}^- (\Sigma^-)\) equilibrium attributes is somewhat limited to the ab \textit{initio} B3LYP studies by Pascoli [33] and Garand et al. [29] who reported \(r_e(\text{C}–\text{C})/r_e(\text{C}–\text{N}) = 1.344 \pm 1.207 \text{ Å}\). Recent MRCE/Q(AQ)Z calculations by Franz et al. [34] put better constraints on these values \((1.360 \text{ and } 1.212 \text{ Å})\). Indeed, our predicted equilibrium rotational constant, \(B_e\), of 11903.44 MHz for the main isotopologue is \(\approx 1\%\) lower and greater than the corresponding DFT [130,139] \((12015.49 \text{ MHz})\) and MRCI [131] \((11820.70 \text{ MHz})\) values, respectively, and is expected to be the most reliable theoretical estimate currently available. With inclusion of vibrational (zero-point level) corrections via the VPT2-based \(\alpha_i^0\)'s, \(B_e\) is found to decrease by \(41.52 \text{ MHz} (B_0 = 11861.91 \text{ MHz})\), consistent with an increase in the vibrationally-averaged \(r_0\) bond distances; similar trends follow for the linear rare isotopologues (Table 2). Note that, for \(\ell-\text{CCN}^-\) and \(\ell-\text{CC}^{15}\text{N}^-\), the calculated \(B_0\) constants, 11369.30 and 11490.06 MHz, show large isotopic shifts (as expected), being \(\approx 430 \text{ MHz}\) smaller on average than the predicted \(B_0\) for \(\ell-\text{CCN}^–\). Thus, differently from \(\ell-\text{CNC}^-\) \(\text{(see Table 2)}\), their pure rotational spectra should be clearly distinguished from that of the main isotopologue. Also quoted in Table 2 are the associated effective rotational constants for the three vibrational fundamentals, \(B_i\) \((i=1-3)\); see also Figure 2 for mode descriptions.

The corresponding spectroscopic attributes obtained for \(\ell-\text{CNC}^- (\Sigma^-)\) using our best composite QFF and VPT2 are presented in Table 3, wherein the most accurate results from the literature [60] are also listed for comparison. Accordingly, the predicted equilibrium \(\text{N}–\text{C}\) bond distance and \(\text{C}–\text{N}–\text{C}\) angle are \(1.356664 \text{ Å} \text{ and } 64.746\)°, respectively. Again, these values are quite close (as expected) to the ones employed as starting reference geometry \((1.355716 \text{ Å} \text{ and } 64.789\text{°})\) and to those reported from the CcCR QFF \((1.356422 \text{ Å} \text{ and } 64.759\text{°})\) [30]. As clearly perceived from Table 3, \(\ell-\text{CNC}^- (\Sigma^-)\) is representative of a (near-oblate) asymmetric top with \(A_e = 43528.50, B_e = 39908.19\) and \(C_e = 20819.90 \text{ MHz}\), values that differ by less than \(0.05\%\) from those predicted by the CcCR protocol [30]; the largest discrepancy \((\text{up to } \approx 20 \text{ MHz})\) is found for \(A_e\) as this appears to be the most sensitive to electron correlation [30]. Using the effective rotational constants for the zero-point level \((A_0, B_0, \text{ and } C_0)\), the calculated Ray’s asymmetry parameters \([15,29,30]\), \(\kappa\), for the main isotopologue are thus 0.675 (this work) and 0.674 (CcCR), hence further suggesting the nearly statistical equivalence of these two theoretical data sets. The corresponding \(\kappa\) values calculated here for \(\ell-\text{CCN}^-\) and \(\ell-\text{CC}^{15}\text{N}^-\) are 0.563 and 0.824, respectively. So, as expected, substitution by \(^{13}\text{C}\) or \(^{15}\text{N}\) makes the corresponding ground-state vibrationally-averaged structures deviate further from or even closer to the oblate symmetric top limit \((\kappa = +1\text{})\), respectively. As in the case of the linear form, clear differences should then be apparent in the pure rotational spectra of \(\ell-\text{CNC}^-\) and its rare isotopologues. For all these species and for future reference, we also collect in Table 3 the theoretically-predicted effective rotational constants for the three vibrational fundamentals, \(A_i, B_i\) and \(C_i\) with \(i = 1-3\).

Also listed in Tables 2 and 3 are the calculated dipole moments, \(\mu_e\), at the QFF equilibrium geometries for the various isotopologues; these were obtained using CC/ACVXZ \((X = T, Q, 5)\) energies and the CBS extrapolation protocol of Ref. [29]. Note that, with the exception of \(\text{C}^{13}\text{N}^-\), all dipoles are oriented along the neg-
The (hyperfine) interaction between the $^{14}$N electric quadrupole moment $[Q(14\text{N}) = 0.02044\text{bar}^{105}]$ and the molecular electric field gradient at $^{14}$N (EFG with principal-axis components $\gamma_z^{14}\text{N} > |\gamma_{y}^{14}\text{N}| > |\gamma_{x}^{14}\text{N}|$) is herein defined by two additional parameters: the nuclear quadrupole coupling constant, $eQ(14\text{N}) \propto (1^{14}\text{N})|\gamma_{z}^{14}\text{N}|$, and the asymmetry parameter, $\eta(14\text{N}) = |\gamma_{x}^{14}\text{N}} - |\gamma_{y}^{14}\text{N}|/|\gamma_{z}^{14}\text{N}|^{107-109}$, see Table 2 and 3. Note that, similarly to $\mu_{e}$, the relevant EFG tensors have been computed via finite field calculations in MOLPRG, with the corresponding CC/ACVXZ ($X = Q, 5$) raw energies being likewise extrapolated to the CBS limit prior to the energy derivative evaluation.$^{28}$ Again, for benchmark purposes, $^{14}$N hyperfine parameters were derived for the parent CNT$^{-}(-\Sigma^{-})$ and $\ell$-C$_{3}$N$^{-}(-\Sigma^{-})$ species using the above protocol and compared with available experimental data.$^{110-111}$ The calculated (observed) $eQ(14\text{N})$'s are $-4.265\text{MHz} (-4.238 \pm 0.032\text{MHz}^{110})$ and $-3.253\text{MHz} (-3.248 \pm 0.005\text{MHz}^{114,115}$), respectively; our theoretical values for $\ell$-CCN$^{-}(-\Sigma^{-})$ and c-CNC$^{-}(1\text{A}_{1})$ are $-2.909$ and 5.099 MHz. Note that, for $\ell$-CCN$^{-}(-\Sigma^{-})$, an additional effect arises due to the intrinsic magnetic (hyperfine) interactions between nuclei with nonzero spin (e.g., $^{14}$N, $^{15}$N, $^{13}$C) and the spin of the unpaired electrons. Such an electron spin-nuclear spin coupling has been shown to dominate the observed hyperfine structure of small open-shell $\Sigma$ species.$^{112}$ The corresponding magnetic hyperfine parameters, i.e., the isotropic Fermi contact ($b_{F}$) and anisotropic spin dipolar ($c_{ij}$) interaction constants,$^{112}$ at specific nucleus are listed in Table 2. These were computed at the full-valence CASCCF/AVQZ level in DALTON.$^{103}$ Suffice it to add that, for both $\ell$-CCN$^{-}(-\Sigma^{-})$ and c-CNC$^{-}(1\text{A}_{1})$, the contributions of other magnetic coupling tensors, e.g., nuclear spin-rotation, amount to only a few kHz; for completeness, they are gathered in Table S5. As emphasized later in section 4, the consideration of all such (hyper)fine structure provides an additional spectroscopic identity to C$_{2}$N$^{-}$ that might be fairly handy for its unambiguous detection.

### 3.3 (Hyper)fine splittings

To aid in future high-resolution laboratory investigations on C$_{2}$N$^{-}$, we also provide in Tables 2 and 3 reliable estimates of fine and hyperfine coupling constants,$^{39}$ see also Table S5. For $\ell$-CCN$^{-}(-\Sigma^{-})$, the calculation of the relevant spin-spin coupling at the QFF equilibrium geometry, $\lambda_{s} = \lambda_{S_{O}} + \lambda_{S_{S}}$, followed the formalism of Vahtras et al.$^{29}$ where $\lambda_{S_{O}}$ is the contribution due to second-order spin-orbit (SO) effects, while $\lambda_{S_{S}}$ describes the magnetic dipole-dipole (electron) spin-spin (SS) interactions.$^{29}$ In turn, the estimation of the (electron) spin-rotation coupling constant ($\gamma_{p}$) relied solely$^{100}$ on its approximate relation to the electronic $g$-tensor as derived by Curt.$^{101}$ $\gamma_{p} = -2B_{e}\Delta g_{zz}$, where $\Delta g_{zz}$ is the transversal component of the calculated $g$-shift$^{102}$ and $B_{e}$ the rotational constant; all such fine structure attributes were herein obtained at the full-valence CASSCF/AVQZ level of theory using DALTON software suite.$^{103}$ To assess the reliability of such an approach, we have applied it to the isoelectronic $\ell$-CCO(3$\Sigma^{+}$) species for which accurate experimental $\lambda_{s}$ and $\gamma_{p}$ values are available.$^{104}$ The calculated constants, $\lambda_{s} = 11594.05\text{MHz}$ and $\gamma_{p} = -15.04\text{MHz}$, are in excellent agreement with the observed values.$^{104}$ 11600 and $-17.82\text{MHz}$, and this is the accuracy one might expect for $\ell$-CCN$^{-}(-\Sigma^{-})$; note here the expectedly small dependence of $\lambda$ and $\gamma$ on zero-point vibrational correction.$^{104,105}$ As noted previously for O$_{2}(3\Sigma_{g}^{+})$, $\ell$-CCO(3$\Sigma^{+}$)$^{104}$ and actually the case here, $\lambda_{s}/\gamma_{p}$ is of the order of $B_{e}/\gamma_{p}$; see Table 2.

Table 4 reports the fundamental vibrational frequencies (in cm$^{-1}$) for $\ell$-CCN$^{-}(-\Sigma^{-})$ isotope using our final composite QFF (Table 2) and SPECTRO/DVR3D.

| Molecule | Description                  | Mode | Harmonic VPT2$^{a}$ | VAR$^{b}$ |
|----------|------------------------------|------|--------------------|----------|
| $\ell$-CCN$^{-}$ | $\sigma$C–N stretch         | $v_1$ | 1759.9            | 1695.6   |
|          | $\pi$C–C–N bend             | $v_2$ | 458.3             | 451.9    |
|          | $\sigma$C–C stretch         | $v_3$ | 1055.5            | 1046.9   |
|          | zero-point energy            | ZPE  | 1866.0            | 1851.0   |

$^{a}$ This work. Data obtained using SPECTRO and the internal-coordinate force field.

$^{b}$ This work. Data obtained using the variational (VAR), exact kinetic energy nuclear motion code DVR3D and the QFF transformed into a Morse-sine coordinate system.

### 3.4 Fundamental vibrational frequencies

Tables 4 and 5 report the fundamental vibrational frequencies of $\ell$-CCN$^{-}(-\Sigma^{-})$ and c-CNC$^{-}(1\text{A}_{1})$ computed with VPT2/VAR and the composite force fields. Also shown for comparison are the corresponding harmonic frequencies and available results from the literature.$^{100}$ As seen, the agreement between VPT2 and exact variational calculations is excellent, with differences being less than 3 cm$^{-1}$. This is not surprising given the absence of large-amplitude fundamental modes and the existence of moderate mode-mode couplings (Table 5), features that clearly justify a VPT2 treatment.$^{50,53}$ Yet, as noted elsewhere$^{71}$ discrepancies between VPT2 and VAR may quickly appear for overtones and combination bands as their energy levels and associated wavefunctions naturally sample larger sections of the molecular PESs that may not be properly described by internal-coordinate QFFs and perturbation theory. In this context, the use of variational approaches in conjunction with Morse-cosine (sine) PESs/QFFs becomes even more critical$^{71}$.

As Tables 4 and 5 show, the computed VPT2 anharmonic zero-
Calculated harmonic and anharmonic vibrational frequencies (in cm\(^{-1}\)) for c-CNC\(^{-}\) (\(\Lambda_4\)) isotopologues using our final composite QFF (Table 3 and SPECTRO/DVR3D).

| Molecule | Description | Mode | Harmonic | VPT2\(^a\) | VPT2\(^b\) | VAR\(^c\) |
|----------|-------------|------|----------|-----------|-----------|----------|
| c-CNC\(^-\) | \(\sigma_1\) C–N symm. stretch | \(\nu_1\) | 1493.7 | 1461.5 | 1462.9 | 1460.3 |
| | \(\sigma_1\) C–N–C bend | \(\nu_2\) | 1011.9 | 990.2 | 991.7 | 993.6 |
| | \(\beta\) C–N antisymm. stretch | \(\nu_3\) | 1068.8 | 1045.5 | 1049.4 | 1046.4 |
| | zero-point energy | ZPE | 1787.2 | 1777.5 | 1780.6 | 1778.1 |
| c-\(^{13}\)CNC\(^-\) | \(\nu_1\) | 1476.1 | 1444.7 | 1446.2 | 1443.5 |
| | \(\nu_2\) | 997.1 | 976.0 | 977.5 | 979.3 |
| | \(\nu_3\) | 1054.3 | 1031.6 | 1035.5 | 1032.5 |
| | ZPE | 1763.8 | 1754.3 | 1757.4 | 1754.9 |
| c-C\(^{15}\)NC\(^-\) | \(\nu_1\) | 1475.1 | 1443.6 | 1445.0 | 1442.6 |
| | \(\nu_2\) | 1002.9 | 981.6 | 983.1 | 984.9 |
| | \(\nu_3\) | 1057.0 | 1034.3 | 1038.1 | 1035.2 |
| | ZPE | 1767.5 | 1758.0 | 1761.1 | 1758.6 |

\(^a\) This work. Data obtained using SPECTRO\(^{40}\) and the internal-coordinate force field.
\(^b\) Ref. 40
\(^c\) This work. Data obtained using the variational (VAR), exact kinetic energy nuclear motion code DVR3D\(^{59}\) and the QFF transformed into a Morse-cosine coordinate system.

Anharmonic constants (in cm\(^{-1}\)) of \(\ell\)-CCN\(^{-}\) (\(\Sigma^+\)) and c-CNC\(^{-}\) (\(\Lambda_4\)) isotopologues.

| \(\ell\)-CCN\(^{-}\) | \(\ell\)-CCN\(^{-}\) | \(\ell\)-CC\(^{13}\)CN\(^{-}\) | \(\ell\)-CC\(^{15}\)N\(^{-}\) | c-CNC\(^{-}\) | c-\(^{13}\)CNC\(^{-}\) | c-\(^{15}\)NC\(^{-}\) |
|------|------|------|------|------|------|------|
| \(x_{11}\) | –27.000 | –27.016 | –25.866 | –26.135 | –5.225 | –5.200 | –5.015 |
| \(x_{12}\) | –10.483 | –10.371 | –9.675 | –10.585 | –16.993 | –16.125 | –17.421 |
| \(x_{13}\) | 0.277 | –0.783 | 2.233 | –0.850 | –26.625 | –25.918 | –25.574 |
| \(x_{22}\) | 0.996 | 0.954 | 0.910 | 1.042 | –4.757 | –4.752 | –4.443 |
| \(x_{23}\) | –7.004 | –6.735 | –6.832 | –6.912 | –7.369 | –6.984 | –7.473 |
| \(x_{33}\) | –8.489 | –7.724 | –8.986 | –8.068 | –3.193 | –3.134 | –3.126 |
| \(x_{22}\) | –0.623 | –0.582 | –0.557 | –0.674 |

\(^a\) This work. Data determined from our final composite internal-coordinate QFFs (Table 1) using second-order perturbation theory\(^{52}\) as implemented in SPECTRO\(^{40}\). Note that, in deriving the above experimental value for \(v_2\) in \(\ell\)-CCN\(^{-}\), the photoelectron spectroscopic data of Garand et al.\(^{39}\) were used (see peaks A and c therein) in combination with the revisited \(\ell\)-CCN\(^{-}\) (\(\Sigma^+\)) (000) \(\Pi_{1/2} - (010)\) \(\mu\Sigma\) energy splitting reported by Muzangwa and Reid\(^{29}\). As for c-CNC\(^{-}\) (\(\Lambda_4\)), the vibrational band origins here computed with VPT2 and our composite force field are in reasonable agreement with those reported from the CcCR QFF\(^{50}\), see Table 5. The largest discrepancy (of up to \(\sim 4\text{cm}^{-1}\)) is found for the C–N asymmetric stretch (\(v_1\)), a trend that becomes already clear at the harmonic level (\(\omega_0\)), hence being probably better explained by the observed variance of the corresponding diagonal quadratic force constant \(F_{13}\) (Table 1). As noted previously, such disparities are undoubtedly attributed to the HO corrections [Eq. (12)]. Our best estimates place the fundamental band origins of c-CNC\(^{-}\) (\(\Lambda_4\)) at 1460.3 (\(v_1\)), 993.6 (\(v_2\)), and 1046.4 cm\(^{-1}\) (\(v_3\)). It is thus hoped that the results here presented aid in future high-resolution laboratory experiments and hopefully astronomical observations of C\(_2\)N\(^-\) as briefly surveyed.

According to Table 4, our best (variational) results for the \(\ell\)-CCN\(^{-}\) (\(\Sigma^+\)) fundamentals are 1696.5 (\(v_1\)), 452.1 (\(v_2\)), and 1045.8 cm\(^{-1}\) (\(v_3\)). Most evidently, the calculated VPT2 and VAR \(v_2\) (C–C–N bend) frequencies are shown to match nearly perfectly the corresponding experimental estimate of \(452.9 \pm 2.9\text{cm}^{-1}\), exhibiting errors of only \(\leq 1\text{cm}^{-1}\); see Table 4. This is undoubtedly an asset of the present composite \textit{ab initio} energy scheme.
Table 7: Selected low-\(J\) (hyperfine) transitions of \(ℓ\)-CCN\(^{-}(\Sigma^{-})\) and \(c\)-CNC\(^{-}(\Sigma^{-})\) in their ground vibrational states and their expected uncertainties; see the marked lines in Figure 4. The corresponding instruments capable of detecting them are also surveyed.

| \(ℓ\)-CCN\(^{-}(\Sigma^{-})\) | Transition\(^a\) | Frequency(MHz) | Uncertainty\(^b\) (MHz) | Instrument\(^c\) |
|---|---|---|---|---|
| \(N'_{c}F'(F'')\) \(\leftarrow\) \(N''_{c}F''(F''')\) | | | | |
| \(1_{2}(4) \leftarrow 0_{1}(2)\) | 22869 | 15 | GBT |
| \(2_{1}(4) \leftarrow 1_{3}(3)\) | 47082 | 29 | ALMA band 1/GBT |
| \(3_{2}(5) \leftarrow 2_{4}(4)\) | 70961 | 44 | GBT |
| \(4_{3}(6) \leftarrow 3_{5}(5)\) | 94754 | 58 | ALMA band 3/GBT |
| \(5_{4}(7) \leftarrow 4_{6}(6)\) | 118514 | 73 | |

| \(c\)-CNC\(^{-}(\Sigma^{-})\) | Transition\(^a\) | Frequency(MHz) | Uncertainty\(^b\) (MHz) | Instrument\(^c\) |
|---|---|---|---|---|
| \(J'_{E,K_{E}}F'(F'')\) \(\leftarrow\) \(J''_{E,K_{E}}F''(F''')\) | | | | |
| \(2_{01}(3) \leftarrow 2_{11}(3)\) | 26919 | 17 | GBT |
| \(2_{11}(3) \leftarrow 2_{02}(3)\) | 57621 | 36 | GBT |
| \(1_{11}(2) \leftarrow 0_{11}(1)\) | 64028 | 40 | GBT |
| \(2_{02}(3) \leftarrow 1_{11}(2)\) | 101135 | 63 | ALMA band 3/GBT |
| \(3_{13}(4) \leftarrow 2_{23}(3)\) | 144956 | 90 | ALMA band 4 |
| \(4_{24}(5) \leftarrow 3_{34}(3)\) | 185944 | 115 | ALMA band 5 |
| \(5_{35}(6) \leftarrow 4_{45}(3)\) | 239192 | 148 | ALMA band 6 |

\(^a\) Only the most intense hyperfine components are reported.

\(^b\) Estimated uncertainties in the predicted transition frequencies. The calculations assume that the theoretical \(A_{N_{0}}\), \(B_{N_{0}}\), and \(C_{N_{0}}\) constants are accurate to within 0.062\% (on average) of experiment (Table S3) so that their computed errors are \(\Delta A_{N_{0}} = \epsilon A_{N_{0}},\Delta B_{N_{0}} = \epsilon B_{N_{0}},\) and \(\Delta C_{N_{0}} = \epsilon C_{N_{0}}\) with \(\epsilon = 6.2 \times 10^{-4}\). For \(ℓ\)-CCN\(^{-}\), the calculated uncertainties in the transition frequencies are \(\approx 2\nu \Delta m_{0}\) (see text and Ref. 115) while for \(c\)-CNC\(^{-}\) they are estimated using \(\Delta A_{N_{0}},\Delta B_{0}\) and \(\Delta C_{0}\) and the energy formulae given in Table 7.7 (page 245) of Ref. 25.

\(^c\) ALMA band 1 is still under construction.

\(\Delta\) ASTROPHYSICAL IMPLICATIONS

Figure 4 shows the simulated rotational spectra of \(ℓ\)-CCN\(^{-}(\Sigma^{-})\) and \(c\)-CNC\(^{-}(\Sigma^{-})\) at 10 K using PGOPHER\(^{115}\) and the spectroscopic parameters presented in Tables 2, 3, and S5; these are \(A_{0}, B_{0}\) and \(C_{0}\) for the rotational constants and equilibrium values for the centrifugal distortion, fine and hyperfine parameters (see text). Working frequency ranges (in GHz) of the GBT and ALMA [from left to right: band 1 (both panels), and bands 3-6 (panel (a)) and bands 3-8 (panel (b))] are also displayed. The insets show the expected hyperfine splitting patterns for selected low-frequency transitions; blue dash-dotted lines highlight their positions without consideration of hyperfine couplings. Lines marked with '*' are listed in Table 7 in increasing order of their frequencies.

As Figure 4 (a) evinces, the rotational spectrum of \(ℓ\)-CCN\(^{-}\) is characteristic of a linear \(\Sigma\) species, where each rotational level (except the one with \(N = 0\)) is split into \(F_{1}(J = N + 1), F_{2}(J = N)\) and \(F_{3}(J = N - 1)\) fine structure components by the presence of the electron spin-spin (\(\lambda\)) and spin-rotation (\(\gamma\)) interactions.\(^{115}\) Here, \(J\) and \(N\) are total angular momentum quantum numbers including and excluding electron spin, respectively; accurate energy formulae for such \(F\) spin-triplets in terms of \(J, N, \lambda\) and \(\gamma\) were given by Schlapp.\(^{115}\) As noted elsewhere,\(^{117}\) and clearly perceived here, rotational transitions among \(F_{1}\) components show greater line strengths than those within the \(F_{2}\) or \(F_{3}\) ladders; see marked lines in Figure 4 (a) and Table 7. Inclusion of hyperfine interactions via electron spin-nuclear spin (\(bf, c\)), \(^{14}\)N quadrupole (\(cQ_{0}\)), and nuclear spin-rotation (\(c\)) cause additional intricate splittings in the observed spectrum as the inset of Figure 4 (a) portrays. These characteristic spectral signatures arising from its intrinsic (hyper)fine structure may indeed offer an extra diagnostic tool to identify this species, notably in radioastronomical studies.
line surveys conducted at conceivably congested frequency domains like in the centimeter/millimeter-wave region (3-300GHz). Note that, for simplicity, in Table 7, only the most intense hyperfine sub-component $F_1$ transitions are reported; the corresponding lower and upper states are identified by their total angular momentum quantum numbers including nuclear spin, $F''$ and $F'$. To further assess the reliability of our theoretical predictions for $\ell$-CCN$^-$ ($^2\Sigma^-$), we again resort to the isoelectronic $\ell$-CCO($^2\Sigma^-$) species. Using its spectroscopic constants calculated by the methods described here (sections 2 and 3), the corresponding synthetic rotational spectrum at 10 K has been so generated and compared with the simulated experimental one; see Figure S3. The results have shown that our approach is capable of reproducing the well-known interstellar $\ell$-CCO lines $1_2 \leftarrow 0_1$ (22258.2 MHz) and $2_3 \leftarrow 1_2$ (45826.7 MHz) detected in TMC-1 [117] to within 17 and 33 MHz of experiment, respectively, hence posing reliable constraints on the expected errors for $\text{C}_2\text{N}^-$; see Table 7. Such an accuracy should be sufficient to initiate astronomical line surveys on this nitrile anion, even when within the uncertainty range other and possibly unassigned transitions are found. Of course, because the uncertainties in the theoretically predicted line frequencies scale roughly as $\sim 2\Delta\nu\Delta\theta_0$ [\Delta\theta_0 is the error in the computed rotational constant (Table 7)], one would expect to find the least deviations in the low-$N$ (low-frequency) range of the spectrum, i.e., in the centimeter and lower end of the millimeter-wave regions (\lesssim 150GHz). Note, however, that, despite influencing the predicted (low-resolution) peak positions, such uncertainties are expected to have little effect on the overall hyperfine splitting patterns reported herein.

As for the $c^-$-CNC$^-$ asymmetric top, the predicted spectral distribution at 10 K and its most intense lines all fall within the centimeter/millimeter-wave range, hence being likewise amenable to radio observations; see Figure 4 (b). Owing to the intrinsic nature of its dipole moment ($\mu$ lies in the $b$ principal axis which in turn coincides with $C_2$), the pure rotational spectrum of $c^-$-CNC$^-$ is characterized by $b$-type transitions for which $\Delta K_a = \pm 1$ and $\Delta K_c = \pm 1$ – the quantum numbers $K_a$ and $K_c$ refer to the projection of $J$ along the molecules’ figure axis in the oblate and prolate limits, respectively. Moreover, because the two equivalent off-axis $C$ atoms are bosons, only half of the rotational levels exist, those with $K_a + K_c$ even. As Figure 4 (b) and Table 7 show, the most intense lines of such occur in the $Q$- and $R$-branches. Inclusion of hyperfine $^{14}\text{N}$ quadrupole and spin-rotation couplings have the expected effects on the observed spectrum, with the predicted splitting pattern for the lowest frequency intense transition $2_{20} \leftarrow 2_{11}$ being shown in the inset of Figure 4 (b). Again, such intrinsic (hyper)fine structure undoubtedly convey an additional influence to the underlying species that might be extremely useful to circumvent spectral line confusion, hence enabling its unambiguous identification in space.

Apart from the likely detectability of $\ell^-$-CCN$^-$ and $c^-$-CNC$^-$ in the radio band with GBT, ALMA, and, possibly, 4GREAT onboard the Stratospheric Observatory for Infrared Astronomy, SOFIA) at higher excitation $T$’s (Figure S2), astronomical searches in the mid-/long-infrared (IR) should also reveal, if abundant, these molecules’ rovibrational signatures. Indeed, their predicted band origins (Tables 4 and 5) are within the instrument ranges of the Echelon-Cross-Echelle Spectrograph (EXES) onboard the SOFIA ($\approx 2200$–$350$ cm$^{-1}$) as well as MIRI, the Mid-InfraRed Instrument for the James Webb Space Telescope (JWST) to be launched later this year. The present study and the highly accurate theoretical data supplied herein will certainly assist in such spectral surveys, thus paving the way for their unequivocal identification both in the laboratory and in space.

Apart from the main isotopologues, the data presented herein for the singly-substituted $^{13}\text{C}$- or $^{15}\text{N}$-bearing variants and their intrinsic (mass-shifted) spectral signatures (including hyperfine structure) add considerably to our $\text{C}_2\text{N}^-$ observational tool kit. These species could significantly contribute to the spectral richness of line surveys and their eventual detection would undoubtedly convey additional information on $\text{C}_2\text{N}^-$ formation pathways and chemical fractionation effects [114] as well as help in gaining extra knowledge on the physical conditions (densities, temperatures and timescales) characteristic of the environment in which they form; this is the case for the recently identified rare isotopologues of complex organic molecules [118].

5 Conclusions

Observations of large, highly-dipolar carbon chain anions in a variety of interstellar environments have helped in establishing the grounds on which our current knowledge of ISM anion chemistry is based. The question remains as to whether the smallest congeners indeed play a role and, if so, how they are formed [22,30,131,132]. Studying the astronomical abundance of even smaller anions, e.g., $\text{C}_2\text{H}^-$, $\text{CH}^-$, $\text{C}_2\text{H}^-$, $\text{CN}^-$, and $\text{C}_2\text{N}^-$, for which REA to their parent neutrals appears to be an unlikely formation pathway, should then help in providing the answers. Advancing this research undoubtedly requires accurate knowledge of their spectroscopic signatures, which for the case of $\text{C}_2\text{N}^-$ are as yet largely absent. Prompted by such a pursuit and by the recent experimental findings by Chacko et al. [33] in this work, we provide such data for both ground $\ell^-$-CCN$^-$ ($^2\Sigma^-$) and low-lying $c^-$-CNC$^-$ ($^1\Delta_1$) forms using state-of-the-art rovibrational quantum chemical techniques. Special efforts are put into the computation of their QFFs by means of a high-level CC-based composite energy scheme that includes extrapolations to both (all-electron) one-particle and (approximate) $\mathcal{X}$-particle basis set limits, in addition to relativistic effects. The final analytic QFFs were then obtained in the usual fashion by least-squares fit, affording composite equilibrium geometries and final force constants with unprecedented accuracy. With these PESs, nuclear motion calculations have then been carried out using both perturbation theory and exact variational methods. Besides standard rovibrational spectroscopic constants and anharmonic vibrational frequencies, the computed data set of properties includes fine and hyperfine interaction constants evaluated ab initio at the QFF equilibrium geometries and is expected to embrace the most reliable theoretical estimates to date for $\text{C}_2\text{N}^-$; similar attributes are also provided for the $^{13}\text{C}$ and $^{15}\text{N}$ singly-substituted isotopologues. The spectroscopic parameters so found can be readily introduced as guesses in standard experimental data reduction analyses through effective Hamiltonians. On the basis of the benchmark calculations per-
formed anew for a minimal test set of prototypical triatomics, the present protocol is shown to rival well-established methodologies currently available in the literature, producing rotational constants and vibrational fundamentals to within ~0.1% and ~0.3% of experiment, respectively, for species with at least two heavy atoms. This preliminary assessment thus allows for a systematic evaluation of the expected uncertainties for C₂N⁻. By relying on their presumably similar electronic structure, comparisons are particularly made with the isoelectronic ℓ-CCO(1Σ⁺) radical for which accurate gas-phase experimental data are available. Specifically for ℓ-CCN⁻(1Σ⁻), the calculated v₂ bending frequency is shown to reproduce its associated experimental estimate to better than 1 cm⁻¹. Such accuracies reported herein should be sufficient for astronomical line surveys on C₂N⁻. Using the theoretically-predicted spectroscopic constants, the rotational spectra of both ℓ-CCN⁻(1Σ⁻) and ℓ-CNC⁻(1A₁) are derived and the predicted transitions frequencies are further compared with working frequency ranges of powerful astronomical facilities such as GBT and ALMA. Our best theoretical estimate places ℓ-CNC⁻(1A₁) at about 15.3 kcal mol⁻¹ above ℓ-CCN⁻(1Σ⁻) which might limit its (astro)chemical synthesis to higher-temperature environments such as in circumstellar envelopes of evolved stars and in the atmosphere of Titan.

**Conflicts of interest**

There are no conflicts to declare.

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**References**

1. A. Dalgarno and R. A. McCray, *ApJ*, 1973, **181**, 95–100.
2. P. Sarre, *J. Chim. Phys.*, 1980, **77**, 769–771.
3. E. Herbst, *Nature*, 1981, **289**, 656–657.
4. B. A. McGuire, *ApJS*, 2018, **179**, 17.
5. P. M. Solomon and W. Klemperer, *ApJ*, 1972, **178**, 389–422.
6. W. D. Watson and E. E. Salpeter, *ApJ*, 1972, **174**, 321–340.
7. W. D. Watson and E. E. Salpeter, *ApJ*, 1972, **175**, 659–671.
8. E. Herbst and W. Klemperer, *ApJ*, 1973, **185**, 505–534.
9. A. Dalgarno and J. H. Black, *Rep. Prog. Phys.*, 1976, **39**, 573–612.
10. Y. Morisawa, H. Hoshina, Y. Kato, Z. Simizu, S. Kuma, N. Sogoshi, M. Fushitani, S. Watanabe, Y. Miyamoto, T. Momose, Y. Kasai and K. Kawaguchi, *PASJ*, 2005, **57**, 325–334.
11. M. C. McCarthy, C. A. Gottlieb, H. Gupta and P. Thaddeus, *Astrophys. J.*, 2006, **652**, L141–L144.
12. J. Simons, *J. Phys. Chem. A.*, 2008, **112**, 6401–6511.
13. M. Larsson, W. D. Geppert and G. Nyman, *Rep. Prog. Phys.*, 2012, **75**, 066901.
14. R. C. Fortenberry, *J. Phys. Chem. A.*, 2015, **119**, 9941–9953.
15. T. J. Millar, C. Walsh and T. A. Field, *Chem. Rev.*, 2017, **117**, 1765–1795.
16. Cernicharo, J., Marcelino, N., Pardo, J. R., Agüinde, M., Terceiro, B., de Vicente, P., Cabezas, C. and Bermúdez, C., *A&A*, 2020, **641**, L9.
17. R. P. A. Bettens and E. Herbst, *ApJ*, 1996, **468**, 686–693.
18. S. Petrie and E. Herbst, *ApJ*, 1997, **491**, 210–215.
19. R. Terzieva and E. Herbst, *Int. J. Mass Spectrom.*, 2000, **201**, 135–142.
20. T. J. Millar, E. Herbst and R. P. A. Bettens, MNRAS, 2000, **316**, 195–203.
21. T. J. Millar, C. Walsh, M. A. Cordiner, R. N. Chuimín and E. Herbst, *ApJ*, 2007, **662**, L87–L90.
22. E. Herbst and Y. Osamura, *ApJ*, 2008, **679**, 1670–1679.
23. C. Walsh, N. Harada, E. Herbst and T. J. Millar, *ApJ*, 2009, **700**, 752–761.
24. F. Güthe, M. Tulej, M. V. Pachkov and J. P. Maier, *ApJ*, 2001, **555**, 466–471.
25. F. Carelli, M. Satta, T. Grassi and F. A. Gianturco, *ApJ*, 2013, **774**, 97.
26. F. Carelli, F. A. Gianturco, R. Wester and M. Satta, *J. Chem. Phys.*, 2014, **141**, 054302.
27. C. Desfrancois, H. Abdoul-Carmine and J. P. Schermann, *Int. J. Mod. Phys. B.*, 1996, **10**, 1339–1395.
28. M. Tulej, D. A. Kirkwood, M. Pachkov and J. P. Maier, *ApJ*, 1998, **506**, L69–L73.
29. S. Petrie, MNRAS, 1996, **281**, 137–144.
30. M. A. Cordiner and T. J. Millar, *ApJ*, 2009, **697**, 68–78.
31. Agüinde, M., Cernicharo, J., Guélin, M., Kahan, C., Roueff, E., Klos, J., Aoiz, F. J., Lique, F., Marcelino, N., Goicoechea, J. R., González García, M., Gottlieb, C. A., McCarthy, M. C. and Thaddeus, P., *A&A*, 2010, **517**, L2.
32. M. A. Cordiner and S. B. Charnley, *ApJ*, 2012, **749**, 120.
33. F. A. Gianturco, M. Satta, E. Yurtsever and R. Wester, *ApJ*, 2017, **850**, 42.
34. E. Yurtsever, M. Satta, R. Wester and F. A. Gianturco, *J. Phys. Chem. A.*, 2020, **124**, 5098–5108.
35. B. Eichelberger, T. P. Snow, C. Barckholz and V. M. Bierbaum, *ApJ*, 2007, **677**, 1283–1289.
36. R. Chacko, S. Banhatti, M. Nrisimhamurty, J. K. Yadav, A. K. Gupta and G. Aravind, *ApJ*, 2020, **905**, 90.
37. M. Nakajima, *J. Mol. Spectrosc.*, 2017, **331**, 106–108.
38. G. Pascoli and H. Lavendy, *Chem. Phys. Lett.*, 1999, **312**, 333–340.
39. E. Garand, T. I. Yacovitch and D. M. Neumark, *J. Chem. Phys.*, 2009, **130**, 064304.
40. R. C. Fortenberry, T. J. Lee and X. Huang, *Phys. Chem. Chem. Phys.*, 2017, **19**, 22860–22869.
41. J. Franz, B. P. Mant, L. González-Sánchez, R. Wester and F. A. Gianturco, *J. Chem. Phys.*, 2020, **152**, 234303.
42. J. K. Anderson and L. M. Ziurys, *Astrophys. J.*, 2014, **795**, L1.
43. J. Grant Hill, A. Mitruschkenov, K. E. Yousaef and K. A. Pe-
98 C. Puzzarini, J. F. Stanton and J. Gauss, *Int. Rev. Phys. Chem.*, 2010, **29**, 273–367.
99 O. Vahtras, O. Loboda, B. Minaev, H. Ågren and K. Ruud, *Chem. Phys.*, 2002, **279**, 133–142.
100 G. Tarczay, P. G. Szalay and J. Gauss, *J. Phys. Chem. A*, 2010, **114**, 9246–9252.
101 R. F. Curl, *Mol. Phys.*, 1965, **9**, 585–597.
102 M. Engström, B. Minaev, O. Vahtras and H. Ågren, *Chem. Phys.*, 1998, **237**, 149–158.
103 K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman et al., *DALTON, A Molecular Electronic Structure Program, Release Dalton2021.alpha* (2020), see: [http://daltonprogram.org](http://daltonprogram.org)
104 Z. Abusara, M. Dehghani and N. Moazzen-Ahmadi, *Chem. Phys. Lett.*, 2006, **417**, 206–210.
105 G. Cazzoli, V. Lattanzi, T. Kirsch, J. Gauss, B. Tercero, J. Cernicharo and C. Puzzarini, *A&A*, 2016, **591**, A126.
106 P. Pyykkö, *Mol. Phys.*, 2018, **116**, 1328–1338.
107 J. M. Lehn and J. P. Kintzinger, in *Nitrogen-14 Nuclear Quadrupole Effects*, ed. M. Witanowski and G. A. Webb, Springer US, Boston, MA, 1973, pp. 79–161.
108 A. Aerts and A. Brown, *J. Chem. Phys.*, 2019, **150**, 224302.
109 H. Linnartz, T. Motylewski, F. Maiwald, D. Roth, F. Lewen, I. Pak and G. Winnewisser, *Chem. Phys. Lett.*, 1998, **292**, 188–192.
110 C. A. Gottlieb, S. Brünken, M. C. McCarthy and P. Thaddeus, *J. Chem. Phys.*, 2007, **126**, 191101.
111 P. Thaddeus, C. A. Gottlieb, H. Gupta, S. Brünken, M. C. McCarthy, M. Agúndez, M. Guélin and J. Cernicharo, *ApJ*, 2008, **677**, 1132–1139.
112 J. A. J. Fitzpatrick, F. R. Manby and C. M. Western, *J. Chem. Phys.*, 2005, **122**, 084312.
113 C. M. Western, *J. Quant. Spectrosc. Radiat. Transf.*, 2017, **186**, 221–242.
114 C. M. R. Rocha and H. Linnartz, *A&A*, 2021, **647**, A142.
115 R. Schlapp, *Phys. Rev.*, 1937, **51**, 342–345.
116 D. Zhao, K. D. Doney and H. Linnartz, *ApJ*, 2014, **791**, L28.
117 M. Ohishi, H. Suzuki, S-I. Ishikawa, C. Yamada, H. Kanamori, W. M. Irvine, R. D. Brown, P. D. Godfrey and N. Kaifu, *ApJL*, 1991, **380**, L39.
118 D. E. Woon, *The Astrochymist*, [http://astrochymist.org/astrochymist_isotopologues.html](http://astrochymist.org/astrochymist_isotopologues.html)