

High-level ab initio quartic force fields and spectroscopic characterization of C_2N^-

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Electronic Supplementary Information

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Summary

- 1) SPECTRO input for ℓ -CCN $^{-}$ ($^3\Sigma^{-}$)
- 2) SPECTRO input for c -CNC $^{-}$ (1A_1)
- 3) Parameters employed in the rovibrational DVR3D calculations
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- 9) PGOPHER file for c -CNC $^{-}$ (1A_1)
- 10) Simulated rotational spectra of ℓ -CCO($^3\Sigma^{-}$) at $T=10$ K

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Table S1: Parameters employed in the rovibrational DVR3D calculations ^a.

Parameter	ℓ -CCN ⁻ (³ Σ ⁻)	c -CNC ⁻ (¹ A ₁)
NPNT1 ^b	40	40
NPNT2 ^b	56	56
NALF ^c	80	80
$r_{e,1}/a_0$ ^d	2.5689	2.7454
$D_{e,1}/E_h$	0.1145	0.2099
$w_{e,1}/E_h$	0.0057	0.0056
$r_{e,2}/a_0$	3.5591	2.1653
$D_{e,2}/E_h$	0.2179	0.3375
$w_{e,2}/E_h$	0.0085	0.0080

^a Jacobi coordinates have been employed throughout. Radial and angular bases are represented by Morse oscillator-like functions and (associated) Legendre polynomials, respectively. The same parameters are utilized for the rare isotopologues.

^b Number of DVR points in r_i ($i = 1, 2$) from Gauss-(associated) Laguerre quadrature.

^c Number of DVR points in θ from Gauss-(associated) Legendre quadrature.

^d $r_{e,i}$, $D_{e,i}$ and $w_{e,i}$ are the equilibrium separation, fundamental frequency and dissociation energy of the relevant coordinate r_i ($i = 1, 2$), respectively.

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Table S2: Internal coordinate force constants for $c\text{-H}_2\text{O}(^1A_1)$, $\ell\text{-HCN}(^1\Sigma_g^+)$, and $\ell\text{-CCO}(^3\Sigma^-)$ model systems taken from our final composite QFFs [Eqs. (2) and (7) of the manuscript]. Units are $\text{mdyn}\text{\AA}^{-n}\text{rad}^{-m}$ appropriate for an energy unit of $\text{mdyn}\text{\AA}(\equiv \text{aJ})$. See Eqs. (3)-(6) in the original paper for the coordinates.

	$c\text{-H}_2\text{O}(^1A_1)^{\text{a}}$	$\ell\text{-HCN}(^1\Sigma_g^+)^{\text{b}}$	$\ell\text{-CCO}(^3\Sigma^-)^{\text{b}}$
F_{11}	8.357 866	18.757 097	15.547 305
F_{21}	0.365 540	-0.206 468	1.119 727
F_{22}	0.703 251	6.251 244	6.323 650
$F_{33/44}$	8.563 429	0.264 816	0.291 883
F_{111}	-41.7268	-125.5625	-113.1874
F_{211}	-0.6029	-0.0316	-1.6699
F_{221}	-0.4480	0.1053	-1.4711
$F_{331/441}$	-41.5576	-0.7204	-0.8905
F_{222}	-0.6955	-35.7840	-44.2481
$F_{332/442}$	0.3912	-0.1820	-0.5236
F_{1111}	181.89	679.57	669.36
F_{2111}	-0.47	-0.05	1.79
F_{2211}	0.30	-0.95	0.57
$F_{3311/4411}$	182.22	0.27	0.70
F_{2221}	0.87	-0.64	5.75
$F_{3321/4421}$	-1.23	0.35	1.80
F_{2222}	-0.81	185.04	212.77
$F_{3322/4422}$	-0.76	0.07	-1.17
$F_{3333/4444}$	183.44	0.89	2.29
F_{3344}		0.65	1.15
$r_{e,1}/\text{pm}$	95.755 605	115.257 717	115.751 957
$r_{e,2}/\text{pm}$	95.755 605	106.478 534	136.313 026
$\angle_e/^\circ$	104.513 727	180.000 000	180.000 000

^a Force constants in symmetry-internal displacement coordinates [Eq. (6) of the manuscript].

^b Force constants in simple internal displacement coordinates [Eqs. (3)-(5) of the manuscript].

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Table S3: Vibrationally-averaged rotational constants (in MHz) for c -H₂O(¹A₁), l -HCN(¹Σ_g⁺), and l -CCO(³Σ⁻) model systems as obtained from our final QFFs (Table S2) and second-order perturbation theory (SPECTRO).

Molecule	Rotational constant				
		QFF	Experiment ^a	Diff. ^b	% Error ^c
c -H ₂ O(¹ A ₁)	A_0	832 984.7	835 755.4	2770.8	0.332
	B_0	434 963.8	434 974.9	11.1	0.003
	C_0	278 375.8	278 414.3	38.5	0.014
l -HCN(¹ Σ _g ⁺)	B_0	44 352.4	44 316.0	36.5	0.082
	B_1	44 035.5	44 003.5	32.0	0.073
	B_2	44 450.9	44 422.4	28.4	0.064
	B_3	44 051.6	44 013.8	37.8	0.086
l -CCO(³ Σ ⁻)	B_0	11 553.2	11 545.6	7.6	0.066
	B_1	11 463.7	11 453.5	10.2	0.089
	B_2	11 595.2	11 587.7	7.5	0.064
	B_3	11 489.0	11 479.6	9.5	0.083
Average ^d				271.8	0.087
Average w/o A_0 H ₂ O ^e				21.9	0.062

^a Refs. 1, 2, 3, 4.

^b Absolute deviations between theory and experiment.

^c Percent errors calculated using (|Diff. |/Experiment) × 100%.

^d Average quantities including all data.

^e Average quantities without inclusion of water A_0 .

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Table S4: Fundamental vibrational frequencies (in cm^{-1}) for $c\text{-H}_2\text{O}(^1A_1)$, $l\text{-HCN}(^1\Sigma_g^+)$, and $l\text{-CCO}(^3\Sigma^-)$ model systems as predicted from our final QFFs (Table S2) and second-order perturbation theory (SPECTRO).

Molecule	Vibrational band origin				
	QFF	Experiment ^a	Diff. ^b	% Error ^c	
$c\text{-H}_2\text{O}(^1A_1)$	ν_1	3653.7	3656.7	2.9	0.081
	ν_2	1595.9	1594.6	1.3	0.079
	ν_3	3751.9	3755.8	3.9	0.104
$l\text{-HCN}(^1\Sigma_g^+)$	ν_1	3309.1	3311.5	2.4	0.072
	ν_2	714.8	713.5	1.4	0.193
	ν_3	2100.3	2096.8	3.4	0.163
$l\text{-CCO}(^3\Sigma^-)$	ν_1	1978.9	1970.9	8.1	0.409
	ν_2	385.6	379.5	6.1	1.608
	ν_3	1066.2	1066.8	0.6	0.058
Average ^d			3.3	0.307	

^a Refs. 1, 2, 3, 4.

^b Absolute deviations between theory and experiment.

^c Percent errors calculated using $(|\text{Diff.}|/\text{Experiment})\times 100\%$.

^d Average quantities including all data.

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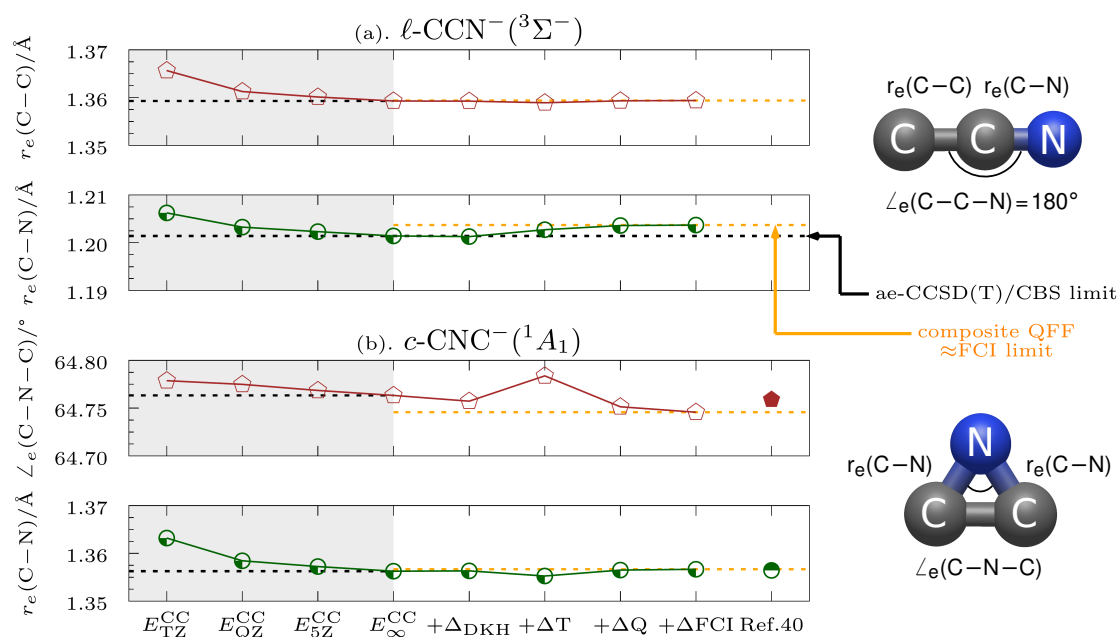


Figure S1: Convergence of the predicted equilibrium geometries for (a). $l\text{-CCN}^- (^3\Sigma^-)$ and (b). $c\text{-CNC}^- (^1A_1)$ as a function of each energy increment [see Eq. (7) of the paper]. For comparison, we also show the calculated values from the raw CC/ACVXZ ($X = T, Q, 5$) QFFs separately as well as the most accurate results from the literature (Ref. 40 of the paper) for the $c\text{-CNC}^-$ species [panel (b)]. Shaded gray areas mark the transition region from one-particle to \mathcal{N} -particle expansion extrapolations. Black and orange lines highlight the corresponding geometries obtained at the one-particle CBS limit (E_{∞}^{CC}) and from the final QFFs, respectively; ae stands for all electron (non-frozen-core) values.

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Table S5: Calculated nuclear spin-rotation interaction constants (**C** tensors) at the QFF equilibrium geometries for ℓ -CCN $^-$ ($^3\Sigma^-$) and c -CNC $^-$ (1A_1). Data obtained at the full-valence CASSCF/AV5Z level of theory using DALTON. Units are kHz.

	ℓ -CCN $^-$	ℓ - ^{13}C CCN $^-$	ℓ -C 13 CN $^-$	ℓ -CC ^{15}N $^-$
$c_I(^{14}\text{N})^a$	1.8802	1.8020(5.9405)	1.8802(5.6409)	(2.5547)
	c -CNC $^-$	c - ^{13}C CNC $^-$	c -C ^{15}N C $^-$	
$C_{aa}(^{14}\text{N})^a$	18.8880	18.5770(36.7986)	(-25.3831)	
$C_{bb}(^{14}\text{N})^a$	14.3623	13.8507(36.9602)	(-20.1467)	
$C_{cc}(^{14}\text{N})^a$	-04762	-0.4630(-0.4177)	(0.6543)	

^a Data evaluated at the ^{14}N nucleus. The corresponding values obtained at ^{13}C and ^{15}N are given in parenthesis.

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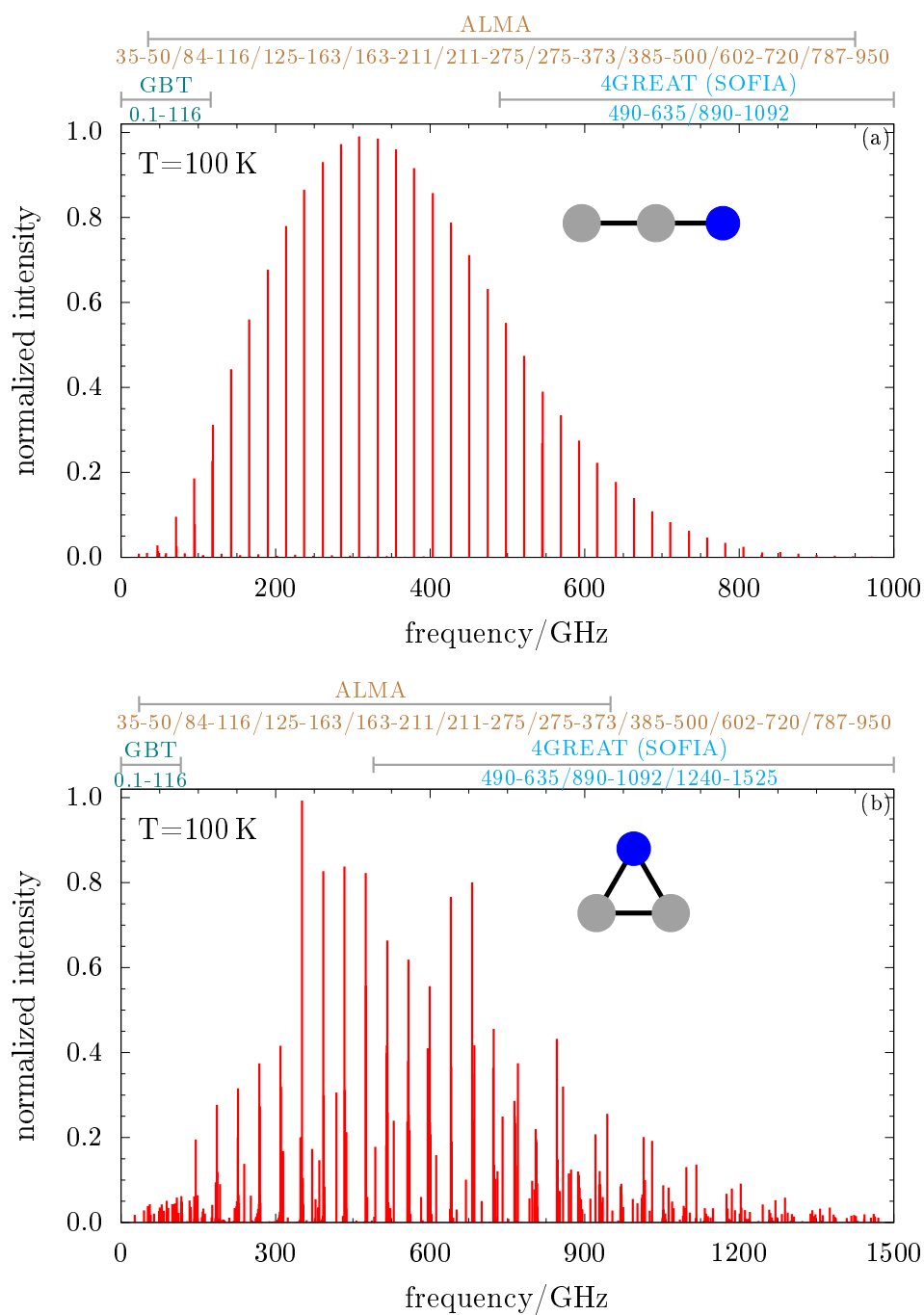


Figure S2: Simulated rotational spectra at $T = 100$ K of (a). $l\text{-CCN}^- (^3\Sigma^-)$ and (b). $c\text{-CNC}^- (^1A_1)$ in their ground vibrational states. Working frequency ranges (in GHz) of the GBT, ALMA (from left to right: band 1, and bands 3 to 10) and the GREAT receiver bands (onboard the Stratospheric Observatory for Infrared Astronomy, SOFIA) are also displayed.

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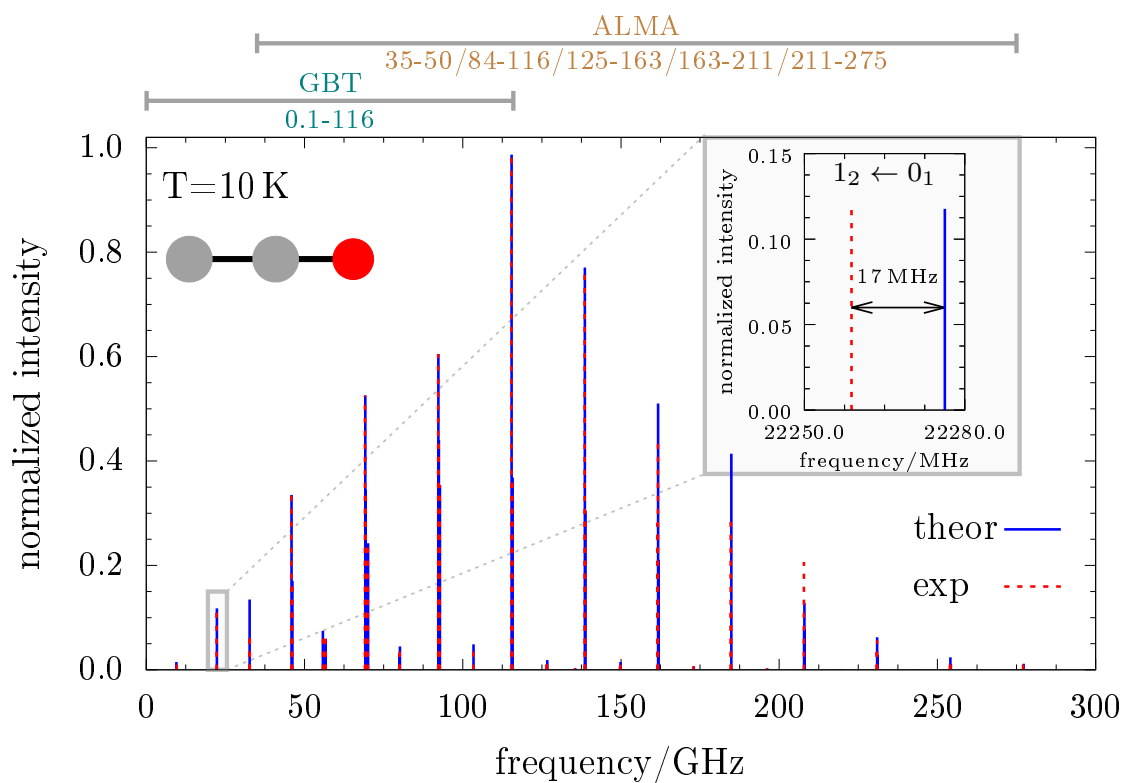


Figure S3: Simulated rotational spectra at 10 K of $l\text{-CCO}(^3\Sigma^-)$ in its ground vibrational state. The spectroscopic constants calculated in this work have been utilized in the theoretical simulation. They are: $B_0 = 11553.212\text{ MHz}$, $D = 0.005586297\text{ MHz}$, $H = -1.311221 \times 10^{-9}\text{ MHz}$, $\lambda = 11594.05\text{ MHz}$, and $\gamma = -15.04\text{ MHz}$. The corresponding experimental values can be found in Ref. [3]. Working frequency ranges (in GHz) of the GBT and ALMA (from left to right: band 1, and bands 3 to 6) are also displayed.

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References

- [1] W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24**, 1139 (1956).
- [2] G. C. Mellau, B. P. Winnewisser, and M. Winnewisser, *J. Mol. Spectrosc.* **249**, 23 (2008).
- [3] Z. Abusara, M. Dehghani, and N. Moazzen-Ahmadi, *Chem. Phys. Lett.* **417**, 206 (2006).
- [4] N. Ohashi, R. Kiryu, S. Okino, and M. Fujitake, *J. Mol. Spectrosc.* **157**, 50 (1993).