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# Computed spectroscopic properties of HCN, HNC, and all their D, <sup>13</sup>C, and <sup>15</sup>N substituted isotopologues

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## ABSTRACT

Starting from *ab initio* electronic structure data, we develop parametrized analytic potential energy surfaces for the HCN and HNC isomers by variationally calculating rovibrational energy levels and adjusting the potential parameters so as to get agreement with experimentally derived transition frequencies to within about 1 cm<sup>-1</sup>. We also determine an analytic expression in terms of molecular parameters to effortlessly calculate the rovibrational energy levels. We use the obtained empirical potentials to calculate rovibrational levels for eight isotopologues of HCN and eight of HNC up to about 4000 cm<sup>-1</sup> above the ground state. The energy levels are estimated to be accurate to within about 3 cm<sup>-1</sup> based on comparison to experimental rovibrational transition frequencies for H<sup>12</sup>C<sup>14</sup>N, H<sup>12</sup>C<sup>14</sup>N, H<sup>13</sup>C<sup>14</sup>N, and H<sup>12</sup>C<sup>15</sup>N. For all 16 isotopologues, we calculate the zero-point energy and in nine cases we can compare with experimentally derived values. In these comparisons, the variationally obtained ZPE is within 5 cm<sup>-1</sup> of the experimentally derived value, while the closed expression gives values within 6 cm<sup>-1</sup> of the experimental values. For all 16 isotopologues, we also give molecular parameters from which the energy levels can easily be calculated using the closed expression. Endo- and exoergicities are given for 12 isotopic exchange reactions involving HCN/HNC and some isotopologues together with pre-exponential factors that should be useful in future modelling studies of rare isotopologues.

**Key words:** astrochemistry – molecular data – molecular processes – ISM: molecules.

## 1 INTRODUCTION

The HCN/HNC isomers were amongst the first detected interstellar molecules (Buhl & Snyder 1970; Snyder & Buhl 1971, 1972) in radioastronomical millimetre observations. HNC was there tentatively identified from theoretical quantum mechanical calculations before two independent experimental confirmations by Blackman et al. (1976) and Saykally et al. (1976). These observations were followed by the fully unexpected detection of DCN by Jefferts, Penzias & Wilson (1973), which initiated a new domain of research, as the corresponding DCN/HCN ratio was inferred to be about 10<sup>-2</sup>, about three orders of magnitude more abundant than expected from the D/H elemental ratio of about 10<sup>-5</sup>. The mid-infrared window corresponding to the  $\nu_2$  band of HCN/HNC and their isotopologues is now also available to highly spectrally resolved astronomical observations thanks to the Echelon–Cross–Echelle–Spectrograph aboard the Stratospheric Observatory for Infrared Astronomy (SOFIA) and corresponding detections of HCN, H<sup>13</sup>CN, and HNC have been reported towards the Orion hot core by Nickerson et al. (2021), whereas HCN and H<sup>13</sup>CN are found in the circumstellar envelope of Y Canum Venaticorum (Fonfría et al. 2021).

On the experimental side, detailed rovibrational spectroscopic studies have been undertaken on the HCN/HNC system (Yang, Rogaski & Wodtke 1990; Romanini & Lehmann 1993; Quapp et al. 1994; Mellau, Winnewisser & Winnewisser 2008; Maki et al. 1995, 1997, 2000; Mellau 2010b, a, 2011c, b, a; Hofmann, Eifert & Mellau 2010), but these concern the main isotopologues (i.e. H<sup>12</sup>C<sup>14</sup>N and H<sup>14</sup>N<sup>12</sup>C) and some deuterated and <sup>13</sup>C or <sup>15</sup>N substituted compounds (Quapp et al. 1999). In addition to the rovibrational levels located in the HCN/HNC potential minima, highly excited rovibrational levels located at and even above the HCN–HNC isomerization potential barrier were observed (up to 23 000 cm<sup>-1</sup> with respect to the vibrationless level of HCN). These experimental works were challenged and complemented by extensive theoretical studies by Makhnev et al. (2018a).

In this paper, we consider all possible HCN/HNC isotopologues, thereby extending previous theoretical studies, by using the potential energy surface (PES) provided by Makhnev et al. (2018b) for HCN and generating additional electronic structure data for HNC. We build empirical PESs in the vicinity of the equilibrium structures of HCN/HNC by computing expansion coefficients of a polynomial for representing the PESs as functions of the bond coordinates in order to reproduce the available observed fundamental bands, combination bands and overtones up to 4000 cm<sup>-1</sup> above the vibrational ground state. We then derive the corresponding spectroscopic constants, allowing us to describe the rovibrational structural pattern of all

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possible isotopic substitutions with D,  $^{13}\text{C}$ , and  $^{15}\text{N}$  in their first vibrationally excited levels. We subsequently compute the corresponding zero-point energies and present some astrophysical applications. The paper is organized as follows. In Section 2, we report the numerical aspects relevant to this study. In Section 3, we present our results and discussions. Then, we draw the main conclusions of this work.

## 2 THEORETICAL AND NUMERICAL ASPECTS

An up-to-date theoretical treatment of HCN and its isotopologues is performed by Makhnev et al. (2018b), who generated an all-electron multireference configuration interaction (MRCI)/aug-cc-pCV6Z PES describing the HCN/HNC minima simultaneously and their isomerization pathway. These authors also included the adiabatic Born–Oppenheimer diagonal correction as well as a relativistic correction. The resulting PES was later used to deduce the pattern of the rovibrational energy levels up to  $25\,000\text{ cm}^{-1}$  for HCN [inserted in the HITRAN data base (Mellau et al. 2021, 2022)], DCN,  $\text{H}^{13}\text{CN}$ , and  $\text{HC}^{15}\text{N}$ .

In this work, we use, as a starting point, the electronic ground state PES of Makhnev et al. (2018b) as calculated at the MRCI+Q/aug-cc-pCV6Z level of theory that is relevant for the HCN system. In order to describe HNC, we calculated new energy points at the CCSD(T)/aug-cc-pV(5 + d)Z level of theory for the ground electronic state using MOLPRO (Werner et al. 2012; Werner et al. 2020) on a grid in internal coordinates  $(R_1, R_2, \theta)$ . For HCN,  $R_1$ ,  $R_2$ , and  $\theta$  correspond to the HC and CN bond distances and the bond angle, respectively, whereas  $R_1$  and  $R_2$  are the HN and NC bond distances, respectively, in HNC. The vibrational frequencies are computed with the RVIB3 code of Carter & Handy (1984) and Carter et al. (1990). This code requires that the PES is of the form

$$V(R_1, R_2, \theta) = \sum_{ijk} c_{ijk} (R_1 - R_{1,\text{eq}})^i \times (R_2 - R_{2,\text{eq}})^j (\theta - \theta_{\text{eq}})^k, \quad (1)$$

where  $R_{1,\text{eq}}$ ,  $R_{2,\text{eq}}$ , and  $\theta_{\text{eq}}$  refer to the equilibrium geometry of each isomer. We therefore fit the coefficients  $c_{ijk}$  to potential energy data taken from Makhnev et al. (2018b) for HCN and from our MOLPRO calculations for HNC. This is done on small grids in internal coordinates covering energies up to  $6000\text{ cm}^{-1}$ . Indeed, we only aim to reproduce the vibrational frequencies of the studied isotopologues below  $4000\text{ cm}^{-1}$ . Therefore, rather small grids of 50 (HCN) and 83 (HNC) points around the equilibrium geometries are sufficient.

The  $c_{ijk}$  coefficients were optimized with a linear least squares procedure using the SURFIT code (Senekowitsch 1988) until the root mean square deviation between the fitted PES and the *ab initio* data (HNC) or the Makhnev et al. (2018b) potential (HCN) is less than  $1\text{ cm}^{-1}$  at the grid points. The polynomial expansions were in this procedure limited to  $i + j + k \leq 6$  for HCN and  $i + j + k \leq 8$  for HNC, where  $i$ ,  $j$ , and  $k$  are non-negative integers. The fitted potentials for HCN and HNC, obtained as described above, were used as starting points for a manual adjustment procedure where the coefficients  $c_{ijk}$  were empirically optimized until reaching a set of coefficients for each isomer that is able to well reproduce the few available lowest experimental frequencies for the normal isotopologues (i.e.  $\text{H}^{12}\text{C}^{14}\text{N}$  and  $\text{H}^{14}\text{N}^{12}\text{C}$ ).

The adjustment of the coefficients  $c_{ijk}$  was done by employing the RVIB3 code of Carter & Handy (1984) and Carter et al. (1990), which uses a variational treatment of nuclear motions to find the rovibrational levels. There the different couplings of rotational-vibrational and electronic angular momenta and anharmonicity

**Table 1.** Vibrational energy levels ( $\text{cm}^{-1}$ ) for HCN and its  $^{13}\text{C}$  and  $^{15}\text{N}$  substitutions for  $J = K = 0$  for levels with an even number of quanta in the bending mode ( $l_2 = 0$  level) and for  $J = K = 1$  for those having an odd number of quanta in the bending mode ( $l_2 = 1$  level). The assignments ( $\nu_1, \nu_2, \nu_3$ ) refer to H–C stretch, bending and C–N stretch, in that order.

Molecule Level	Ref.	$\text{H}^{12}\text{C}^{14}\text{N}$	$\text{H}^{12}\text{C}^{15}\text{N}$	$\text{H}^{13}\text{C}^{14}\text{N}$	$\text{H}^{13}\text{C}^{15}\text{N}$
(0 0 0)	[1]	0.0	0.0	0.0	0.0
	[2]	0.0	0.0	0.0	0.0
(0 1 0)	[1]	712.17	711.25	706.24	705.32
	[3]	712.00	–	–	–
(0 2 0)	[1]	1411.24	1409.19	1399.81	1397.75
	[2]	1411.42	1409.31	1399.76	–
(0 0 1)	[1]	2096.90	2064.33	2062.79	2029.34
	[2]	2096.85	2064.32	2063.05	–
(0 3 0)	[1]	2113.66	2110.62	2096.82	2093.77
	[3]	2113.49	–	–	–
(0 4 0)	[1]	2803.26	2799.04	2781.36	2777.14
	[2]	2802.96	2798.64	2780.59	–
(0 1 1)	[1]	2805.34	2771.94	2764.54	2730.26
	[3]	2805.57	–	–	–
(1 0 0)	[1]	3311.76	3310.30	3294.32	3292.91
	[2]	3311.48	3310.09	3293.51	–
(0 5 0)	[1]	3496.49	3491.24	3469.61	3464.37
	[3]	3495.2	–	–	–
(0 2 1)	[1]	3501.25	3467.09	3454.42	3419.52
	[2]	3502.12	3467.78	3455.79	–
(0 0 2)	[1]	4172.92	4108.40	4105.14	4038.89
	[2]	4173.07	4108.64	4105.87	–
(0 6 0)	[1]	4177.11	4170.64	4145.56	4139.12
	[2]	4174.61	4167.99	4142.36	–

Note. [1] This work; [2] HCN: Mellau (2011b);  $\text{H}^{13}\text{CN}$  &  $\text{HC}^{15}\text{N}$ : Maki et al. (2000); [3] Varandas & Rodrigues (2006).

effects are fully taken into account, which should ensure that the obtained frequencies are accurate to within  $1\text{ cm}^{-1}$ , if converged, as indicated in Carter & Handy (1984) and Carter et al. (1990). The empirical coefficients obtained in this way for both isomers are listed in Table S1 of the supplementary information. Vibrational energy levels and their respective wave functions for each isomer and its isotopologues are computed for  $J = K = 0$  and  $J = K = 1$ , where  $J$  is the angular momentum quantum number and  $K$  is its projection on the  $z$ -axis. In the RVIB3 calculations, the basis sets include up to 25 unidimensional harmonic oscillator eigenfunctions for the stretching modes and 41 associated Legendre functions for the bending modes. These basis sets ensure convergence of the vibrational levels that we have calculated to within  $0.1\text{ cm}^{-1}$ .

## 3 RESULTS

The HCN/HNC isomers both belong to the  $C_{\infty v}$  point group. They do have three vibrational modes:  $(\nu_1, \nu_2, \nu_3)$  that refer to H–C/H–N stretch, bending and C–N stretch, in that order.  $\nu_1$  and  $\nu_3$  correspond to stretching modes of  $\sigma^+$  symmetry, whereas  $\nu_2$  is a bending mode of  $\pi$  symmetry with a degeneracy of 2. Tables 1–4 give the vibrational levels of the HCN/DCN and HNC/DNC isotopologues as derived from our empirical PESs after variational treatment of the nuclear motion. These tables also report the available experimental data on these species as extracted from the references given in the tables.

The anharmonic wavenumbers of all vibrational levels of  $\text{H}^{12}\text{C}^{14}\text{N}$  and  $\text{H}^{14}\text{N}^{12}\text{C}$  located below  $4200\text{ cm}^{-1}$  differ by less than  $1\text{ cm}^{-1}$  from the experimental ones by construction. Indeed, these energy levels were used to optimize the empirical PESs as stated in Section 2.

**Table 2.** Vibrational energy levels ( $\text{cm}^{-1}$ ) for DCN and its  $^{13}\text{C}$  and  $^{15}\text{N}$  substitutions for  $J = K = 0$  for levels with an even number of quanta in the bending mode ( $l_2 = 0$  level) and for  $J = K = 1$  for those having an odd number of quanta in the bending ( $l_2 = 1$  level). The assignments ( $\nu_1, \nu_2, \nu_3$ ) refer to D–C stretch, bending and C–N stretch, in that order.

Molecule Level	Ref.	D <sup>12</sup> C <sup>14</sup> N	D <sup>12</sup> C <sup>15</sup> N	D <sup>13</sup> C <sup>14</sup> N	D <sup>13</sup> C <sup>15</sup> N
(0 0 0)	[1]	0.0	0.0	0.0	0.0
	[2]	0.0	0.0	0.0	0.0
(0 1 0)	[1]	568.90	567.68	561.25	560.01
(0 2 0)	[1]	1129.17	1126.52	1114.48	1111.80
	[2]	1129.99	–	–	–
(0 0 1)	[1]	1928.26	1902.96	1914.51	1887.83
	[2]	1925.26	–	–	–
(0 3 0)	[1]	1689.76	1685.80	1668.05	1664.06
(0 4 0)	[1]	2242.12	2236.6	2213.93	2208.45
	[2]	2243.96	–	–	–
(0 1 1)	[1]	2502.47	2475.90	2479.91	2451.92
(1 0 0)	[1]	2629.28	2620.36	2589.56	2581.34
	[2]	2630.30	–	–	–
(0 5 0)	[1]	2794.99	2788.18	2760.33	2753.48
(0 2 1)	[1]	3067.45	3039.41	3036.80	3007.31
	[2]	3060.68	–	–	–
(0 0 2)	[1]	3717.48	3706.45	3665.81	3655.50
	[2]	3729.13	–	–	–
(0 6 0)	[1]	3340.01	3331.64	3299.33	3290.94
	[2]	3342.56	–	–	–

Note. [1] This work; [2] Carter, Mills & Handy (1993).

The comparison of our set of data computed for  $\text{H}^{13}\text{C}^{14}\text{N}$  and  $\text{H}^{12}\text{C}^{15}\text{N}$  with the corresponding measured values reveals that a good agreement is also obtained for these isotopologues, where deviations of less  $1 \text{ cm}^{-1}$  are found except for some levels where these deviations may reach  $3 \text{ cm}^{-1}$ . This validates the variational approach adopted here and allows us to calculate the unobserved transitions with an accuracy of  $1\text{--}3 \text{ cm}^{-1}$ . We also point out that the agreement between experiments and theoretical modelling is closer for the least excited levels. We emphasize that experimental data are missing for the rare isotopologues of HNC,  $\text{H}^{15}\text{N}^{12}\text{C}$ ,  $\text{H}^{14}\text{N}^{13}\text{C}$ ,  $\text{H}^{15}\text{N}^{13}\text{C}$ ,  $\text{D}^{14}\text{N}^{12}\text{C}$ ,  $\text{D}^{15}\text{N}^{12}\text{C}$ ,  $\text{D}^{14}\text{N}^{13}\text{C}$ , and  $\text{D}^{15}\text{N}^{13}\text{C}$ .

In order to derive spectroscopic constants, the empirical analytic forms of the  $V(R_1, R_2, \theta)$  potentials were incorporated into perturbative treatments of the nuclear motions. Within perturbation theory  $V(R_1, R_2, \theta)$  is first derived as a quartic force field in internal coordinates and then converted to dimensionless normal coordinates, using  $l$ -tensor algebra (Hoy, Mills & Strey 1972). Afterwards, harmonic frequencies, rotational constants, and vibration-rotation and anharmonicity terms are computed from the derivatives of the potentials at their respective minima, using the second-order perturbation theory formulae derived by Mills, as implemented in the SURFIT code (Mills 1972; Senekowitsch 1988). Spectroscopic constants of each HCN/HNC isotopologue are reported in Tables 5 and 6, using symbols as defined in Herzberg (1991). The energy terms of linear polyatomic molecules, such as HCN and HNC,  $T(\nu_1, \nu_2^l, \nu_3, J)$ , are then defined by Herzberg (1991), Mellau (2011b), and Fuchs et al. (2004):

$$\begin{aligned}
 T(\nu_1, \nu_2^l, \nu_3, J) &= \sum_i \omega_i \left( \nu_i + \frac{d_i}{2} \right) + \sum_i \sum_j x_{ij} \left( \nu_i + \frac{d_i}{2} \right) \left( \nu_j + \frac{d_j}{2} \right) \\
 &+ g_{22} \ell_2^2 + B_v (J(J+1) - D_J [J^2(J+1)^2 - \ell_2^2]), \quad (2)
 \end{aligned}$$

**Table 3.** Vibrational energy levels ( $\text{cm}^{-1}$ ) for HNC and its isotopologues for  $J = K = 0$  for levels with an even number of quanta in the bending mode ( $l_2 = 0$  level) and for  $J = K = 1$  for those having an odd number of quanta in the bending mode ( $l_2 = 1$  level). The assignments ( $\nu_1, \nu_2, \nu_3$ ) refer to H–N stretch, bending and C–N stretch, in that order.

Molecule level	Ref.	H <sup>14</sup> N <sup>12</sup> C	H <sup>15</sup> N <sup>12</sup> C	H <sup>14</sup> N <sup>13</sup> C	H <sup>15</sup> N <sup>13</sup> C
(0 0 0)		0.0	0.0	0.0	0.0
(0 1 0)	[1]	462.98	460.26	462.33	459.61
	[3]	462.75	–	–	–
(0 2 0)	[1]	926.21	920.78	924.68	919.24
	[2]	926.50	–	–	–
(0 3 0)	[1]	1397.57	1389.49	1395.34	1387.26
	[3]	1400.57	–	–	–
(0 4 0)	[1]	1865.55	1854.88	1862.41	1851.72
	[2]	1867.06	–	–	–
(0 0 1)	[1]	2023.89	1998.13	1980.92	1954.43
	[2]	2023.86	–	–	–
(0 5 0)	[1]	2340.77	2327.58	2336.89	2323.69
(0 1 1)	[1]	2478.41	2449.81	2434.99	2405.66
	[3]	2478.49	–	–	–
(0 6 0)	[1]	2810.92	2795.25	2806.08	2790.39
	[2]	2809.29	–	–	–
(0 2 1)	[1]	2933.31	2901.89	2889.22	2857.08
	[2]	2934.82	–	–	–
(0 7 0)	[1]	3288.54	3270.43	3282.90	3264.77
(1 0 0)	[1]	3652.65	3641.01	3651.74	3640.11
	[2]	3652.65	–	–	–

Note. [1] This work; [2] Mellau (2011c); [3] Varandas & Rodrigues (2006).

**Table 4.** Vibrational energy levels ( $\text{cm}^{-1}$ ) for DNC and its isotopologues for  $J = K = 0$  for levels with an even number of quanta in the bending mode ( $l_2 = 0$  level) and for  $J = K = 1$  for those having an odd number of quanta in the bending mode ( $l_2 = 1$  level). The assignments ( $\nu_1, \nu_2, \nu_3$ ) refer to D–N stretch, bending, and C–N stretch in that order.

Molecule level	D <sup>14</sup> N <sup>12</sup> C	D <sup>15</sup> N <sup>12</sup> C	D <sup>14</sup> N <sup>13</sup> C	D <sup>15</sup> N <sup>13</sup> C
(0 0 0)	0.0	0.0	0.0	0.0
(0 1 0)	362.83	359.24	361.91	358.31
(0 2 0)	727.40	720.33	725.35	718.26
(0 3 0)	1095.24	1084.71	1092.20	1081.65
(0 4 0)	1462.83	1448.99	1458.60	1444.73
(0 0 1)	1937.92	1921.90	1898.49	1881.39
(0 5 0)	1832.94	1815.80	1827.67	1810.50
(0 1 1)	2299.39	2279.09	2259.02	2237.65
(0 6 0)	2201.70	2181.41	2195.18	2174.86
(0 2 1)	2661.72	2637.38	2620.36	2594.95
(0 7 0)	2572.72	2549.29	2565.11	2541.66
(1 0 0)	2787.06	2763.75	2782.25	2759.38

where  $\omega_i$  refers to the harmonic frequencies,  $d_i$  is the corresponding degeneracy, and  $x_{ij}$  stands for the anharmonic terms. The sum is performed over the number of vibrational modes. The rotational constants associated to vibrationally excited levels are expressed as  $B_v = B_e - \sum_i \alpha_i (\nu_i + \frac{1}{2})$ .  $D_J$  is the centrifugal distortion term.

These values should be helpful for possible future detections of rare isotopologues.

#### 4 ASTROPHYSICAL IMPLICATIONS

We can derive the zero-point energies (ZPEs) of all isotopologues, which play an important role in isotopic exchange reactions. In

**Table 5.** Spectroscopic constants computed in this work for the HCN isotopologues.

	HCN	HC <sup>15</sup> N	H <sup>13</sup> CN	H <sup>13</sup> C <sup>15</sup> N	DCN	DC <sup>15</sup> N	D <sup>13</sup> CN	D <sup>13</sup> C <sup>15</sup> N
$\omega_1$	3447.7	3446.4	3428.6	3427.5	2707.1	2698.2	2665.5	2657.2
$\omega_2$	725.9	724.9	719.6	718.5	578.9	577.5	570.8	569.5
$\omega_3$	2127.8	2094.3	2093.3	2058.9	1952.3	1926.0	1938.6	1910.9
$x_{11}$	-51.4794	-51.6405	-51.6113	-51.7507	-20.7796	-21.2493	-20.9875	-21.4866
$x_{12}$	-11.2520	-11.1890	-10.7369	-10.6846	-12.0119	-11.8127	-11.0970	-10.8950
$x_{13}$	-13.7969	-13.3170	-12.1653	-11.7624	-31.0527	-29.5819	-28.9817	-27.4294
$x_{22}$	-2.6443	-2.6637	-2.4983	-2.5146	-2.2524	-2.2769	-2.0711	-2.0921
$x_{23}$	-3.2396	-3.0923	-3.81777	-3.6716	4.3281	4.3538	3.1656	3.1725
$x_{33}$	-10.4274	-10.1055	-10.2372	-9.9006	-6.8648	-6.7106	-6.8243	-6.6828
$g_{22}$	5.6690	5.7134	5.5475	5.5895	3.5186	3.5601	3.3451	3.3835
$B_e$	1.4842	1.4409	1.4458	1.4019	1.2115	1.1767	1.1908	1.1554
$10^5 D_J$	0.2846	0.2687	0.2712	0.2555	0.1859	0.1752	0.1793	0.1687
$10^3 q_a$	7.2432	6.8380	6.9349	6.5312	6.0499	5.7208	5.9265	5.5927
$10^3 \alpha_1$	10.4498	10.0376	9.64759	9.2500	10.5697	10.1701	9.9267	9.5285
$10^3 \alpha_2$	-3.9314	-3.7694	-3.51763	-3.3632	-4.6295	-4.4636	-4.2783	-4.1169
$10^3 \alpha_3$	9.9544	9.5476	9.63571	9.2238	6.4341	6.1849	6.3133	6.0653

<sup>a</sup> $q$ :  $\ell$ -doubling constant.

**Table 6.** Spectroscopic constants computed in this work for the HCN isotopologues.

	HNC	HN <sup>13</sup> C	H <sup>15</sup> NC	H <sup>15</sup> N <sup>13</sup> C	DNC	DN <sup>13</sup> C	D <sup>15</sup> N C	D <sup>15</sup> N <sup>13</sup> C
$\omega_1$	3816.7	3816.0	3803.9	3803.3	2879.0	2874.2	2854.3	2850.0
$\omega_2$	465.8	464.9	462.8	462.0	366.1	365.1	362.4	361.3
$\omega_3$	2058.9	2014.6	2032.4	1987.4	1966.4	1925.7	1950.2	1908.4
$x_{11}$	-68.3140	-68.4049	-68.2053	-68.2862	-31.9008	-32.3644	-32.1105	-32.5479
$x_{12}$	-22.7106	-22.6250	-22.1497	-22.0719	-18.6462	-18.3571	-17.6528	-17.3805
$x_{13}$	-11.8060	-12.5901	-11.2305	-12.4238	-20.8395	-19.3902	-19.0427	-17.6750
$x_{22}$	4.8089	4.7866	4.7873	4.7655	2.6417	2.6131	2.6390	2.6118
$x_{23}$	-8.6636	-8.4736	-8.7962	-8.5994	-1.2354	-1.2540	-1.9610	-1.9689
$x_{33}$	-10.0692	-9.3341	-9.8162	-8.9809	-8.2241	-7.9618	-8.2308	-7.9547
$g_{22}$	3.1914	3.2354	3.17912	3.2230	1.5724	1.6119	1.5281	1.5671
$B_e$	1.5120	1.4523	1.4821	1.4219	1.2701	1.2212	1.2533	1.2037
$10^5 D_J$	0.3170	0.2935	0.3060	0.2827	0.2110	0.1954	0.2058	0.1902
$10^3 q^a$	10.4697	9.6779	10.1247	9.3362	9.3971	8.71238	9.2445	8.5531
$10^3 \alpha_1$	10.0656	9.5263	9.4770	8.9514	10.3781	9.82470	9.8352	9.2924
$10^3 \alpha_2$	-5.3308	-4.9800	-4.8087	-4.4726	-7.3017	-6.91154	-6.8324	-6.4510
$10^3 \alpha_3$	10.9600	10.3406	10.6635	10.0418	7.7014	7.30655	7.6109	7.2093

<sup>a</sup> $q$ :  $\ell$ -doubling constant.

Table 7, we report our theoretical estimates obtained from both the variational and the perturbative (equation 2) approaches together with experimentally deduced values when available. These computations give the relative stability of the different isotopologues. The heaviest species has the smallest ZPE, thus the highest dissociation energy and stability.

The variational computations show a closer agreement with the measured values than the perturbative calculations and differences less than  $3 \text{ cm}^{-1}$  are obtained for HCN and HNC, whereas DCN results differ by about  $5 \text{ cm}^{-1}$ . However, when computing differences of ZPEs between isotopologues for the <sup>13</sup>C and <sup>15</sup>N substitutions within the HCN, DCN, HNC and DNC groups, values agree within less than half a wavenumber. Such ZPE information is essential for determining the endothermicity/exothermicity of possible isotopic exchange reactions. The occurrence of an endothermic channel for the inverse isotopic exchange reaction leading to the lighter isotopologue was invoked by Watson (1973, 1974) to explain the significant deuterium enhancement of some molecules. Isotopic fractionation in carbon and nitrogen-containing molecules has been the subject of several recent studies (Roueff, Loison & Hickson 2015; Loison et al. 2019, 2020; Colzi et al. 2020), where isotopic

exchange reactions have been introduced and estimated. We report in Table 8 the reactions involving HCN/HNC and extend the results to additional rare isotopes. We assume the same pre-exponential factor and power-law temperature dependence as in Loison et al. (2020) for the reaction rate coefficients and compute the  $\Delta E$  values from the experiments, when available, and from the present ZPE<sub>1</sub> values, see Table 7, for the other cases. Such reactions should be introduced in future modelling studies. The estimates of  $\Delta E$  for reactions 9, 10, 11, and 12 were obtained using the ZPE values of HCNH<sup>+</sup> and its isotopologues computed by Brites & Jutier (2012).

## 5 CONCLUSION

Based on a PES for HCN developed by Makhnev et al. (2018b) and our own *ab initio* calculations for HNC, we have developed parametrized analytic PESs for these isomers by variationally calculating rovibrational energy levels and adjusting the potential parameters so as to get agreement with experimentally derived transition frequencies to within about  $1 \text{ cm}^{-1}$ . We also use a closed expression in terms of molecular parameters to effortlessly obtain



**Table 7.** ZPE values (in  $\text{cm}^{-1}$ ) for all isotopologues obtained from different approaches. Also shown (in Kelvin) are differences relative to the normal or deuterated isotopologue. ZPE<sub>1</sub>: this work, variational computation; ZPE<sub>2</sub>: this work, perturbative calculation (equation 2); ZPE<sub>3</sub>: derived from experimental results.

Molecule	ZPE <sub>1</sub> ( $\text{cm}^{-1}$ )	ZPE <sub>2</sub> ( $\text{cm}^{-1}$ )	ZPE <sub>3</sub> ( $\text{cm}^{-1}$ )	$\Delta(\text{ZPE}_1)$ (K)	$\Delta(\text{ZPE}_2)$ (K)	$\Delta(\text{ZPE}_3)$ (K)
H <sup>12</sup> C <sup>14</sup> N	3481.69	3484.83	3479.23 <sup>1</sup>	–	–	–
H <sup>13</sup> C <sup>14</sup> N	3449.01	3452.27	3446.63 <sup>1</sup>	47.0	46.8	46.9
H <sup>12</sup> C <sup>15</sup> N	3463.33	3466.68	3460.96 <sup>1</sup>	26.4	26.1	26.3
H <sup>13</sup> C <sup>15</sup> N	3430.29	3433.65	3427.98 <sup>1</sup>	73.9	73.6	73.7
D <sup>12</sup> C <sup>14</sup> N	2888.93	2887.83	2883.89 <sup>2</sup>	–	–	–
D <sup>13</sup> C <sup>14</sup> N	2853.71	2852.61	2848.79 <sup>2</sup>	50.7	50.6	50.3
D <sup>12</sup> C <sup>15</sup> N	2870.05	2869.21	2865.24 <sup>2</sup>	27.2	26.7	26.8
D <sup>13</sup> C <sup>15</sup> N	2834.48	2833.69	2829.81 <sup>2</sup>	78.3	77.8	77.8
H <sup>14</sup> N <sup>12</sup> C	3371.13	3370.17	3369.9 <sup>3</sup>	–	–	–
H <sup>14</sup> N <sup>13</sup> C	3347.97	3346.85	–	33.3	33.5	–
H <sup>15</sup> N <sup>12</sup> C	3348.95	3347.95	–	31.9	32.0	–
H <sup>15</sup> N <sup>13</sup> C	3325.46	3324.36	–	65.7	65.9	–
D <sup>14</sup> N <sup>12</sup> C	2769.28	2766.26	–	–	–	–
D <sup>14</sup> N <sup>13</sup> C	2745.66	2742.93	–	33.9	33.6	–
D <sup>15</sup> N <sup>12</sup> C	2745.39	2742.64	–	34.3	34.0	–
D <sup>15</sup> N <sup>13</sup> C	2721.44	2718.89	–	68.8	68.2	–

Note. (1) Maki et al. (2000); (2) Möllmann et al. (2002); (3) Mellau (2011b).

**Table 8.** <sup>13</sup>C and <sup>15</sup>N isotopic exchange reactions involving HCN and HNC.

Reference /comment	Label	Reaction	$A^a$ ( $\text{cm}^3 \text{s}^{-1}$ )	$\alpha$	$f(B, M)$	$\Delta E$ (K)
(1)	1	<sup>13</sup> C + HCN ⇌ C + H <sup>13</sup> CN	$2.0 \times 10^{-10}$	0	1	46.9
(2)	2	<sup>13</sup> C + HC <sup>15</sup> N ⇌ C + H <sup>13</sup> C <sup>15</sup> N	$2.0 \times 10^{-10}$	0	1	47.5
(2)	3	<sup>13</sup> C + DCN ⇌ C + D <sup>13</sup> CN	$2.0 \times 10^{-10}$	0	1	50.3
(2)	4	<sup>13</sup> C + DC <sup>15</sup> N ⇌ C + D <sup>13</sup> C <sup>15</sup> N	$2.0 \times 10^{-10}$	0	1	51.0
(1)	5	<sup>13</sup> C + HNC ⇌ C + HN <sup>13</sup> C	$3.0 \times 10^{-11}$	0	1	33.3
(2)	6	<sup>13</sup> C + H <sup>15</sup> NC ⇌ C + H <sup>15</sup> N <sup>13</sup> C	$3.0 \times 10^{-11}$	0	1	33.8
(2)	7	<sup>13</sup> C + DNC ⇌ C + DN <sup>13</sup> C	$3.0 \times 10^{-11}$	0	1	33.9
(2)	8	<sup>13</sup> C + D <sup>15</sup> NC ⇌ C + D <sup>15</sup> N <sup>13</sup> C	$3.0 \times 10^{-11}$	0	1	33.8
(1)	9	HCNH <sup>+</sup> + H <sup>13</sup> CN ⇌ H <sup>13</sup> CNH <sup>+</sup> + HCN	$2.0 \times 10^{-09}$	–0.5	1	3.9
(3)	10	HCNH <sup>+</sup> + HC <sup>15</sup> N ⇌ HC <sup>15</sup> NH <sup>+</sup> + HCN	$2.0 \times 10^{-09}$	–0.5	1	10.8
(2)	11	HCNH <sup>+</sup> + D <sup>13</sup> CN ⇌ H <sup>13</sup> CNH <sup>+</sup> + DCN	$2.0 \times 10^{-09}$	–0.5	1	0.3
(2)	12	HCNH <sup>+</sup> + DC <sup>15</sup> N ⇌ HC <sup>15</sup> NH <sup>+</sup> + DCN	$2.0 \times 10^{-09}$	–0.5	1	10.3

<sup>a</sup>The forward reaction rate coefficient  $k_f = A(T/300)^\alpha$ , where  $A$  is a pre-exponential factor. The reverse reaction rate coefficient,  $k_r$ , is obtained by  $k_r = \frac{k_f}{f(B, M)} \times \exp(-\Delta E/T)$ .

(1) Loison et al. (2020), (2) this work, (3) Loison et al. (2019).

the energy levels. The agreement is good but not quite as good as for the variational calculations.

We use the obtained empirical potentials to calculate rovibrational levels for eight isotopologues of HCN and eight of HNC up to about 4000  $\text{cm}^{-1}$  above the ground state. The energy levels are estimated to be accurate to within about 3  $\text{cm}^{-1}$  based on comparison to experimental rovibrational transition frequencies for H<sup>12</sup>C<sup>14</sup>N, H<sup>12</sup>C<sup>14</sup>N, H<sup>13</sup>C<sup>14</sup>N, and H<sup>12</sup>C<sup>15</sup>N. For the other 12 isotopologues, there are no experimental measurements available.

For all 16 isotopologues, we calculate the zero-point energy and in nine cases we can compare with experimentally derived values. In these comparisons, the variationally obtained ZPEs are within 5  $\text{cm}^{-1}$  of the experimentally derived values, while those from the closed expression (equation 2) are within 6  $\text{cm}^{-1}$  of the values derived from experimental data. We also notice that the computed difference of ZPEs between <sup>13</sup>C or <sup>15</sup>N substituted HCN, HNC,

DCN, or DNC main isotopologues agree on the other hand to within 0.3  $\text{cm}^{-1}$ . This remark applies both to the comparison between experiments and theoretical computations as well as to comparison between the two theoretical approaches. This impacts directly the accuracy of the endo-exoergicities of possible isotopic exchange reactions.

For all 16 isotopologues, we give molecular parameters from which the energy levels can easily be calculated using the perturbative energy expression from Herzberg (1991) given in the text above. From the ZPE calculations and the accuracy of the variationally calculated energy levels (relative to the ZPE), we estimate that the energy levels from the closed expression should be accurate to within 10  $\text{cm}^{-1}$  at worst.

Finally, we report endo- and exoergicities for 12 reactions involving HCN/HNC and some isotopologues together with estimated rate constants that we believe will be useful in future modelling studies.

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## DATA AVAILABILITY

All data are incorporated into the article and its online supplementary material.

## REFERENCES

- Blackman G. L., Brown R. D., Godfrey P. D., Gunn H. I., 1976, *Nature*, 261, 395
- Brites V., Jutier L., 2012, *J. Mol. Spectrosc.*, 271, 25
- Buhl D., Snyder L. E., 1970, in *Bulletin of the American Astronomical Society*. p. 299
- Carter S., Handy N. C., 1984, *Mol. Phys.*, 52, 1367
- Carter S., Handy N., Rosmus P., Chambaud G., 1990, *Mol. Phys.*, 71, 605
- Carter S., Mills I. M., Handy N. C., 1993, *J. Chem. Phys.*, 99, 4379
- Colzi L., Sipilä O., Roueff E., Caselli P., Fontani F., 2020, *A&A*, 640, A51
- Fonfría J. P. et al., 2021, *A&A*, 651, A8
- Fuchs U. et al., 2004, *Zeitschrift Naturforschung Teil A*, 59, 861
- Herzberg G., 1991, *Molecular Spectra and Molecular Structure. Vol.2: Infrared and Raman Spectra of Polyatomic Molecules*. Krieger Publishing Company, Malabar, FL
- Hofmann J. P., Eifert B., Mellau G. C., 2010, *J. Mol. Spectrosc.*, 262, 75
- Hoy A. R., Mills I. M., Strey G., 1972, *Mol. Phys.*, 24, 1265
- Jefferts K. B., Penzias A. A., Wilson R. W., 1973, *ApJ*, 179, L57
- Loison J.-C., Wakelam V., Gratier P., Hickson K. M., 2019, *MNRAS*, 484, 2747
- Loison J.-C., Wakelam V., Gratier P., Hickson K. M., 2020, *MNRAS*, 498, 4663
- Makhnev V. Y., Kyuberis A. A., Zobov N. F., Lodi L., Tennyson J., Polyansky O. L., 2018a, *J. Phys. Chem. A*, 122, 1326
- Makhnev V. Y., Kyuberis A. A., Polyansky O. L., Mizus I. I., Tennyson J., Zobov N. F., 2018b, *J. Mol. Spectrosc.*, 353, 40
- Maki A., Quapp W., Klee S., Mellau G. C., Albert S., 1995, *J. Mol. Spectrosc.*, 174, 365

- Maki A., Quapp W., Klee S., Mellau G. C., Albert S., 1997, *J. Mol. Spectrosc.*, 185, 356
- Maki A. G., Mellau G. C., Klee S., Winnewisser M., Quapp W., 2000, *J. Mol. Spectrosc.*, 202, 67
- Mellau G. C., 2010a, *J. Chem. Phys.*, 133, 164303
- Mellau G. C., 2010b, *J. Mol. Spectrosc.*, 264, 2
- Mellau G. C., 2011a, *J. Chem. Phys.*, 134, 194302
- Mellau G. C., 2011b, *J. Chem. Phys.*, 134, 234303
- Mellau G. C., 2011c, *J. Mol. Spectrosc.*, 269, 77
- Mellau G. C., Winnewisser B. P., Winnewisser M., 2008, *J. Mol. Spectrosc.*, 249, 23
- Mellau G. C., Makhnev V. Y., Gordon I. E., Zobov N. F., Tennyson J., Polyansky O. L., 2021, *J. Quant. Spec. Radiat. Transf.*, 270, 107666
- Mellau G. C., Makhnev V. Y., Gordon I. E., Zobov N. F., Tennyson J., Polyansky O. L., 2022, *J. Quant. Spec. Radiat. Transf.*, 279, 108059
- Mills I. M., 1972, in N.Rao K., Mathews C. W., eds, *Molecular Spectroscopy: Modern Research*. Academic, New York
- Möllmann E., Maki A. G., Winnewisser M., Winnewisser B. P., Quapp W., 2002, *J. Mol. Spectrosc.*, 212, 22
- Nickerson S. et al., 2021, *ApJ*, 907, 51
- Quapp W., Klee S., Mellau G. C., Albert S., Maki A., 1994, *J. Mol. Spectrosc.*, 167, 375
- Quapp W., Hirsch M., Mellau G. C., Klee S., Winnewisser M., Maki A., 1999, *J. Mol. Spectrosc.*, 195, 284
- Romanini D., Lehmann K. K., 1993, *J. Chem. Phys.*, 99, 6287
- Roueff E., Loison J. C., Hickson K. M., 2015, *A&A*, 576, A99
- Saykally R. J., Szanto P. G., Anderson T. G., Woods R. C., 1976, *ApJ*, 204, L143
- Senekowitsch J., 1988, PhD thesis, University of Frankfurt, Germany
- Snyder L. E., Buhl D., 1971, *ApJ*, 163, L47
- Snyder L. E., Buhl D., 1972, *Ann. NY Acad. Sci.*, 194, 17
- Varandas A. J. C., Rodrigues S. P. J., 2006, *J. Phys. Chem. A*, 110, 485
- Watson W. D., 1973, *ApJ*, 181, L129
- Watson W. D., 1974, *ApJ*, 188, 35
- Werner H. J. C., Knowles P. J., Knizia G. R. M. F. M. S., 2012, *J. Phys. Chem. A*, 2, 242
- Werner H.-J. et al., 2020, *J. Chem. Phys.*, 152, 144107
- Yang X., Rogaski C. A., Wodtke A. M., 1990, *J. Chem. Phys.*, 92, 2111

## SUPPORTING INFORMATION

Supplementary data are available at *MNRAS* online.

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