Full Spectroscopic Model and Trihybrid Experimental-Perturbative-Variational Line List for CN

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ABSTRACT

Accurate line lists are important for the description of the spectroscopic nature of small molecules. While a line list for CN (an important molecule for chemistry and astrophysics) exists, no underlying energy spectroscopic model has been published, which is required to consider the sensitivity of transitions to a variation of the proton-to-electron mass ratio.

Here we have developed a DUO energy spectroscopic model as well as a novel hybrid style line list for CN and its isotopologues, combining energy levels that are derived experimentally (MARVEL), using the traditional/perturbative approach (MOLLIST), and the variational approach (from a DUO spectroscopic model using standard ExoMol methodology). The final Trihybrid ExoMol-style line list for $^{12}\text{C}^{14}\text{N}$ consists of 28,004 energy levels (6,864 experimental, 1,574 perturbative, the rest variational) and 2,285,103 transitions up to 60,000 cm$^{-1}$ between the three lowest electronic states ($X^2\Sigma^+, A^2\Pi$, and $B^2\Sigma^+$). The spectroscopic model created is used to evaluate CN as a molecular probe to constrain the variation of the proton-to-electron mass ratio; no overly promising sensitive transitions for extragalactic study were identified.

Key words: molecular data – techniques: spectroscopic

1 INTRODUCTION

CN is a molecule ubiquitous in astrochemistry that has been well studied experimentally and theoretically. CN shows initial promise as a potential molecular probe to constrain the variation of the proton-to-electron mass ratio (Syme et al. 2019; Syme & McKemmish 2020a), however an energy spectroscopic model of CN - not currently available - is required to identify key transitions of enhanced sensitivity.

The cyano (CN) radical was the second observed molecular species in the interstellar medium (McKellar 1940) and observed extra-galactically by Henkel et al. (1988). CN is one of the most widely distributed astrophysical molecules observed across the electromagnetic spectrum. For example, in the optical and visible, CN has been seen in interstellar clouds (McKellar 1940; Ritchey et al. 2011a), carbon stars (Barnbaum et al. 1996), and the Hale Bopp comet (Wagner et al. 1997). In infrared, CN has been seen in comets (Huggins et al. 1881; Shinnaka et al. 2017), active galactic nuclei (Riffel et al. 2007), and sunspots (Harvey 1973). In the microwave region CN has been observed in the Orion nebula (Jelferts et al. 1970) and throughout diffuse clouds (Allen & Knapp 1978). CN provides insight into diverse astrophysical phenomena. CN stars (a peculiar type of carbon stars) have unusually strong CN peaks present in their spectra (Barnbaum et al. 1996). CN is often used as a tracer of gas layers which are affected by photochemistry, and is predominantly found in regions exposed to ionizing stellar UV radiation (Riechers et al. 2007). The rotational temperature of CN is used to estimate the brightness of the cosmic microwave background (Ritchey et al. 2011b). CN is an important part of the HCN cycle, a key precursor in the synthesis of prebiotic molecules, such as nucleotides, amino acids, and lipid building blocks (Furtenbacher et al. 2017).

Modelling observations of astronomical or other gaseous environments accurately, and thus understanding these environments, requires high accuracy line lists - i.e. details of all the energy levels in a molecule and the strength of transitions between these levels. These in turn rely on high-quality experimental data. In the case of CN, we need to consider at least the three lowest lying electronic states, the $X^2\Sigma^+$ ground state, the $A^2\Pi$ state at 9243 cm$^{-1}$, and the $B^2\Sigma^+$ state at 25752 cm$^{-1}$, as astrophysical observations of interactions between all of these electronic bands have been observed (Hamano et al. 2019). All available experimental data was recently compiled for $^{12}\text{C}^{14}\text{N}$ (Syme & McKemmish 2020b), which then used the MARVEL (Furtenbacher et al. 2007) procedure to extract empirical energy levels.

For CN, the most accurate available line list is the MOLLIST data (Brooke et al. 2014), which considers transitions between the three lowest electronic states of CN - i.e. the $X^2\Sigma^+$, $A^2\Pi$ and the $B^2\Sigma^+$ states. Uses of the MOLLIST line list have included: constraining the chemical evolution of the local disc with C and N abundances (Botelho et al. 2020), modelling...
the impact of chemical hazes in exoplanetary atmospheres (Lavvas & Arfaux 2021), probing interstellar clouds (Weltz et al. 2020), chemical abundance in stars that may harbour rocky planets from TESS data (Tautvaisienė et al. 2020), as well as observing the first A 2Π-X 2Σ + (0,0) band in the interstellar medium Hamano et al. (2019).

The MOLLIST line list is computed using the so-called traditional model (or perturbative method), fitting experimental transition frequencies to a model Hamiltonian using PGo-pher (Western 2017) to obtain a set of spectroscopic constants which are then used to predict unobserved line frequencies along with ab initio dipole moments, see Brooke et al. (2014) for further details. The MOLLIST traditional model interpolates very accurately but does not extrapolate well because it is based on perturbation theory (Bernath 2020). The CN MOLLIST line list has no published underlying energy spectroscopy model (i.e. set of potential energy and coupling curves) suitable for testing the sensitivity of its molecular transitions to variation in the proton-to-electron mass ratio.

Variational line lists, such as those developed by ExoMol (Tennyson et al. 2020) and TheoReTS (Rey et al. 2016), are based on a spectroscopically fitted energy spectroscopic model - i.e. potential energy and coupling curves. One popular program to create a variational line list for diatomics is the nuclear motion program DUO which variationally solves the nuclear motion Schrodinger equation for coupled electronic states (Yurchenko et al. 2016; Tennyson & Yurchenko 2017). DUO has been successfully utilised to generate spectroscopic data for over 15 diatomic molecules (Tennyson et al. 2020).

These variational line lists 'extrapolate more reliably because [they are] a more realistic and less empirical model' (Bernath 2020), but are not as accurate for each individual vibrionic band due to the reduced number of free parameters and increased physical constraints. No variational line list and thus no energy spectroscopic model exists for CN prior to this paper. This missing spectroscopic model meant that CN could not be rigorously evaluated as a potential molecular probe for proton-to-electron mass variation in Syme et al. (2019).

Experimental accuracy for individual lines (often the strongest lines) can be achieved for traditional and variational line lists by replacing energy levels with experimentally-derived energy levels best obtained from a MARVEL inversion of all experimental transitions.

Both traditional and variational line lists have their advantages. To take best advantage of all diatomic spectroscopic data (reviewed by McKemmish (2021)), we propose here to use a novel trihybrid approach combining data from the traditional and variational approaches with the best available experimental data.

This paper is organised as follows. In Section 2, we describe the creation of the energy spectroscopic model and analyse the resulting variationally predicted energy levels in comparison to MOLLIST and MARVEL energy levels.

In Section 3, we add the intensity spectroscopic model and combine previous line list approaches to develop and explore a novel Trihybrid line list. Finally, in Section 4, we use the newly generated energy spectroscopic model from Section 2 to consider CN as a potential probe to constrain the variation of the proton-to-electron mass ratio, and calculate the sensitivity coefficient of transitions generated by the final spectroscopic model.

### 2 ENERGY SPECTROSCOPIC MODEL (ESM)

#### 2.1 Construction

An energy spectroscopic model (ESM) consists of potential energy curves (PECs) for each electronic state and coupling curves between those states. ESMs for diatomic molecules can be constructed using DUO (Yurchenko et al. 2016; Tennyson & Yurchenko 2017), where each PEC and coupling curves are represented by a mathematical functions.

The parameters of these functions are fit using DUO to minimise the difference between the Duo-predicted variational energy levels and the available MARVEL experimentally-derived energy levels (Syme & McKemmish 2020b). DUO uses a grid-based sinc DVR method to solve the coupled Schrodinger equation; for our calculations, we use grid of uniformly distributed 1001 points from 0.6-4.0 Å. This fit is highly non-linear and so fitting is normally done iteratively, often considering just one electronic or vibrionic state at a time. The  v = 14, 16, and 18 states of the B 2Σ + state were unweighted in the DUO fit due to large perturbations. For further details of the fitting process, see Yurchenko et al. (2016); Tennyson & Yurchenko (2017); Tennyson et al. (2016). Of particular note for CN was the high vibrational and rotational quantum numbers for which experimental data is available; essentially removing the need for ab initio data as a starting point.

During the fitting process we identified a few misassignments in the MARVEL data. The transitions that these data was taken from were identified and removed; the updated MARVEL files are in the supplementary material.

### Potential Energy Curves: The potential energy curves (PEC) for the X 2Σ +, A 2Π, and B 2Σ + electronic states were described using the Extended Morse Oscillator (EMO) (Lee et al. 1999) with standard parameterisation, detailed in Section 2.1. The X 2Σ + and A 2Π state have a common dissociation asymptote fixed to the experimental value of 63,619.4 cm⁻¹ (Huber & Herzberg 1979), whereas the B 2Σ + state has a higher dissociation limit fixed at 82,843.11 cm⁻¹ (Yin et al. 2018). To ensure a sufficient fit, a significant amount
of parameters were used to fit these states due to the large amount of experimental data including very high $v$ and high $J$ energy levels from MARVEL.

The resulting PECs are shown in Figure 1. Calculated \textit{ab initio} curves are provided for reference but not used in the construction of the ESM due to the wealth of available experimental energy levels. The fitted and \textit{ab initio} curves are very similar near the bottom of the potential well, with increasing deviation at larger $r$ because the \textit{ab initio} predicted dissociation energy differed from the experimental value. Our calculations used MRCI/aug-cc-pVTZ level with an (6,2,2,0) active space based on state-averaged ($X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ only) Complete Active Space Self-Consistent Field (SA-CASSCF) calculations. We note that similar \textit{ab initio} results are presented in, for example, Shi et al. (2011); Yin et al. (2018); however, underlying raw data could not be obtained, highlighting the importance of data accessibility (McKemmish 2021).

\textbf{Coupling:} The interaction of electronic states is described through a variety of coupling curves, all described using the Surkus-polynomial expansion (Yurchenko et al. 2016) to ensure correct asymptotic behaviour. Various diagonal and off-diagonal terms were included as part of the fit to the MARVEL energy levels, described in Table 2, with the most important term the diagonal spin-orbit coupling term for the $A^2\Pi$ state.

\subsection{2.2 Analysis}

\textbf{Comparison of variational Duo with experimentally-derived MARVEL energy levels:} Figure 2 visually compares the variational Duo energy levels to the experimentally-derived MARVEL energy levels as a function of energy. The mean, RMSD, and maximum absolute deviation for each vibronic level collated in Table 3. Overall, the $X^2\Sigma^+$ and $A^2\Pi$ states are very well fitted with an overall RMSD of 0.29 cm\(^{-1}\) and 0.21 cm\(^{-1}\) respectively. The $B^2\Sigma^+$ state is more problematic, but the rmsd is still 2.97 cm\(^{-1}\), with errors dominated by the weaker fits in the strongly perturbed higher vibronic levels.

The first 2 panels for figure 2 show the deviation of the $X^2\Sigma^+$ state. We can see that the residuals of the $X^2\Sigma^+$ state are fairly consistent across each vibrational level, with the exception of $v = 17$ which has RMSD greater than 1 cm\(^{-1}\). The maximum absolute deviation from the MARVEL energies in the $X^2\Sigma^+$ state is 3.01 cm\(^{-1}\) in the $v = 17$ state. The $A^2\Pi$ state, shown in panels 3 and 4 show consistent errors for all vibronic states, with no vibronic level having an RMSD greater than 1 cm\(^{-1}\), even the $v = 17$ state, which visibly looks scattered only has a rmsd of 0.67 cm\(^{-1}\). The maximum deviation occurs in the $v = 17$ state, with an absolute deviation of 3.15 cm\(^{-1}\). We see the diverging deviation in the lower vibronic levels of the $A^2\Pi$ state, while small, suggest an issue with the spin-spin coupling.

In the bottom two panels we see the deviation in the $B^2\Sigma^+$ state. While the $B^2\Sigma^+$ state is much higher in energy the deviation from the MARVEL energy levels seems especially large, and scattered. Over half of the vibronic levels in the $B^2\Sigma^+$ state have a RMSD greater than 1 cm\(^{-1}\), and all bar four vibronic levels have an RMSD greater than 0.5 cm\(^{-1}\). The $v = 16$ to $v = 18$ have RMSD greater than 2.0 cm\(^{-1}\). The maximum deviation of 37.95 cm\(^{-1}\) in the $B^2\Sigma^+$ state occurs at $J = 30.5$ and $v = 16$. The poor performance for high $v$ levels in the $B^2\Sigma^+$ state is probably caused by perturbations that are not represented in our spectroscopic model, for example with the spectroscopically dark $4\Sigma^+$ state.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & $X^2\Sigma^+$ & $A^2\Pi$ & $B^2\Sigma^+$ \\
\hline
Diagonal & $-26.5$ & $-7.22$ & \\
$\lambda_{SS}$ & 0.100 & 0.100 & 1.00 \\
$\gamma_{SR}$ & 0.0131 & -0.00370 & 0.0183 \\
$B_{\text{rot}}$ & 0.00162 & -0.00266 & -0.00323 \\
$\lambda_{p2q}$ & 0.0231 & & \\
$\lambda_{opq}$ & & -0.0277 & \\
Off Diagonal & $X$, A & B, A & \\
$\text{SO}$ & 18.8 & 1.90 & \\
$L^+$ & -0.368 & -0.368 & \\
\hline
\end{tabular}
\caption{Fitted constants, as defined in Yurchenko et al. (2016), affecting energy levels of individual electronic states: diagonal spin–spin ($\lambda_{SS}$), spin–rotational ($\gamma_{SR}$), rotational Born-Oppe\-nheimer breakdown term ($B_{\text{rot}}$), spin–orbit (SO), and lambda doubling ($\lambda_{p2q}$, $\lambda_{opq}$) constants in cm\(^{-1}\). Off-diagonal spin-orbit and electronic angular momentum coupling terms respectively.}
\end{table}
Figure 2. Residuals energy differences (in cm$^{-1}$) between the Duo energies and the Marvel empirical energy levels, split into two subfigures for each electronic state. Note the differing vertical scales.
Table 3. Vibronic-scale breakdown of the average deviation of the DUO and MOLLIST energy levels from the MARVEL empirical energy levels. All deviations are in cm⁻¹.

| v   | DUO (this work) - MARVEL | MOLLIST - MARVEL |
|-----|--------------------------|------------------|
| X 2Σ⁺⁺ | Mean | RMSD | |Max| Mean | RMSD | |Max|
| 0   | 97.5 | -0.01 | 0.05 | 0.19 | -0.01 | 0.02 | 0.05 |
| 1   | 99.5 | 0.02  | 0.05 | 0.19 | -0.01 | 0.02 | 0.05 |
| 2   | 97.5 | 0.01  | 0.06 | 0.21 | -0.01 | 0.02 | 0.07 |
| 3   | 81.5 | 0.10  | 0.10 | 0.10 | -0.01 | 0.02 | 0.03 |
| 4   | 72.5 | -0.02 | 0.04 | 0.14 | -0.01 | 0.02 | 0.05 |
| 5   | 60.5 | -0.04 | 0.04 | 0.07 | -0.01 | 0.01 | 0.03 |
| 6   | 48.5 | -0.04 | 0.04 | 0.05 | -0.00 | 0.01 | 0.05 |
| 7   | 36.5 | -0.03 | 0.03 | 0.05 | -0.01 | 0.01 | 0.03 |
| 8   | 34.5 | 0.01  | 0.03 | 0.06 | -0.01 | 0.01 | 0.03 |
| 9   | 30.5 | 0.04  | 0.05 | 0.12 | -0.01 | 0.01 | 0.03 |
| 10  | 27.5 | 0.07  | 0.07 | 0.17 | -0.01 | 0.02 | 0.07 |
| 11  | 36.5 | 0.10  | 0.19 | 0.57 | 0.59 | 1.89 | 5.93 |
| 12  | 19.5 | 0.05  | 0.06 | 0.11 | -0.00 | 0.02 | 0.05 |
| 13  | 23.5 | -0.04 | 0.12 | 0.53 | -0.00 | 0.10 | 0.52 |
| 14  | 37.5 | -0.35 | 0.63 | 2.83 | 0.03 | 0.17 | 0.65 |
| 15  | 22.5 | 0.16  | 0.23 | 0.68 | 0.10 | 0.15 | 0.54 |

A 2Π

Table 3 shows some vibronic bands with significant MOLLIST errors, probably energies that were not included in the MOLLIST initial fit.

Spectroscopic constants: Table 4 compares the equilibrium spectroscopic parameters calculated by DUO for our fitted potential energy curves against existing data (Yin et al. 2018; Shi et al. 2011), including those used to construct MOLLIST. The parameters for the X 2Σ⁺⁺ state agree very well across all sources, with a small difference in ωₑ and ωₓₜₑ in the computational values of Yin et al. (2018). The A 2Π state has similar agreement across the sources, with a small difference of Tₑ values, but a much closer consensus on the ωₑ and ωₓₜₑ values. The B 2Σ⁺⁺ state has the most disagreement across its equilibrium parameters. Our values for ωₑ differ the most, and we see disagreement across all sources for ωₓₜₑ. The difference between the Brooke et al. (2014) spectroscopic constants are our own are unlikely to be the primary reason for the differences in our predicted energy levels. Instead, the defining difference is likely to be the use of band constants in MOLLIST line list.

3 TRHYBRID LINE LIST

A line list contains two files; a states (.states) file which lists all quantum states with their energies and quantum numbers and a transitions (.trans) file which details the strength of the transitions between states.

3.1 Energy Levels

Here we present a novel trihybrib approach for the construction of the final states file that combines energy levels from DUO and MOLLIST with the experimental perturbative variational line list.
Table 4. Spectroscopic equilibrium parameters for the 3 electronic states in the DUO spectroscopic model, compared with select values from the literature.

| Electronic State | Parameter | This work | Brooke et al. (2014)* | Yin et al. (2018) | Huber & Herzberg (1979) | Babou et al. (2009) |
|------------------|-----------|-----------|-----------------------|------------------|------------------------|---------------------|
| X $^2\Sigma^+$  | $T_e$     | 0.0000    | 0                     | 0                | 0                      | 0                   |
|                  | $\omega_e$| 2068.7230 | 2068.68325            | 2069.26          | 2068.59                | 2068.65             |
|                  | $\omega_e\chi_e$ | 13.1808 | 13.12156 | 10.231 | 13.097 | 13.097 | 13.097 |
|                  | $B_0$     | 1.8968    | 1.89978               | 1.9013           | 1.8997                 | 1.899783            |
|                  | $R_e$     | 1.1727    | 1.1718                 | 1.1714           | -                      | 1.1718              |
|                  | $\alpha_e$| 0.0174    | 0.01738               | 0.01719          | 0.01736                | 0.01737             |
| A $^2\Pi$       | $T_e$     | 9247.2180 | 9243.2959            | 9109.95          | 9245.28                | 9240                |
|                  | $\omega_e$| 1812.8320 | 1813.288             | 1814.75          | 1812.56                | 1813.26             |
|                  | $\omega_e\chi_e$ | 12.5944 | 12.77789 | 13.053 | 12.6 | 12.7687 |
|                  | $B_0$     | 1.7205    | 1.7158                 | 1.7174           | 1.7151                 | 1.7159              |
|                  | $R_e$     | 1.2314    | 1.233044              | 1.2324           | -                      | 1.2333              |
|                  | $\alpha_e$| 0.0172    | 0.01725               | 0.01708          | 0.01708                | 0.017167            |
| B $^2\Sigma^+$  | $T_e$     | 25755.5900| 25752.59             | 25767.42         | 25752                  | 25752               |
|                  | $\omega_e$| 2156.2630 | 2162.233             | 2163.04          | 2163.9                 | 2161.46             |
|                  | $\omega_e\chi_e$ | 16.2569 | 19.006 | 14.789 | 20.2 | 18.219 |
|                  | $B_0$     | 1.9732    | 1.96797               | 1.9554           | 1.973                  | 1.96891             |
|                  | $R_e$     | 1.1498    | 1.15133               | 1.151            | 1.15                   | -                   |
|                  | $\alpha_e$| 0.0178    | 0.0188                | 0.01908          | 0.023                  | 0.020377            |

* $\alpha_e$ for Brooke et al. (2014) was the opposite sign for all three states than other sources; we assume a definition difference.

3.2 Intensity Spectroscopic Model

The intensity spectroscopic model consists of diagonal and off-diagonal (transition) dipole moments curves, calculated from high-level $ab$ initio methods then extrapolated within DUO.

Using our state-averaged MRCl/aug-cc-pVTZ calculation methodology discussed above, we calculated all relevant dipole moment curves, shown as circles in Figure 5. This figure also shows the larger basis set results from Brooke et al. (2014) for the X $^2\Sigma^+$-X $^2\Sigma^+$, A $^2\Pi$-X $^2\Sigma^+$ and B $^2\Sigma^+$-X $^2\Sigma^+$ curves as crosses. For our line list, we chose to use these larger basis set calculations for these curves, but note that there is only modest differences between the two $ab$ initio methods (bottom subfigure); the modest impact of this choice on our final line list is discussed in the Supporting Information. We input our selected dipole moment data points as a grid into DUO, which fits a curve to these values.

We validate our $ab$ initio results by comparing against experimental dipole moments. For the X $^2\Sigma^+$ and B $^2\Sigma^+$ states...
Table 5. Extract from the state file for $^{12}$C$^{14}$N. Full tables are available at www.exomol.com and in the Supporting Information.

| n  | $E$ (cm$^{-1}$) | $g_{rot}$ | $J$ | unc | $\tau$ | $g$ | $+/−$ | $e/f$ | State | $v$ | $\Lambda$ | $\Sigma$ | $\Omega$ | Source | $E_{\text{Duo}}$ |
|----|----------------|----------|-----|------|-------|-----|-------|-------|-------|-----|----------|----------|--------|--------|----------|
| 1  | 0.000000       | 6        | 0.5 | 0.001293 | -1.00E+00 | 2.002305 | + | e | X | 0 | 0 | 0.5 | 0.5 | M | 0.000000 |
| 102| 3.777245       | 6        | 0.5 | 0.003132 | 9.99E+04  | -0.667444 | - | f | X | 0 | 0 | -0.5 | -0.5 | M | 3.775090 |
| 81 | 52340.028680   | 6        | 0.5 | 0.500000 | 1.27E-07  | 2.002272 | + | e | B | 15 | 0 | 0.5 | 0.5 | P | 52340.262410 |
| 132| 28904.950010   | 6        | 0.5 | 0.500000 | 5.19E-06  | -0.000931 | - | f | A | 12 | -1 | 0.5 | -0.5 | P | 28904.596730 |
| 78 | 51326.871830   | 6        | 0.5 | 1.000000 | 1.27E-07  | 2.002272 | + | e | B | 15 | 0 | 0.5 | 0.5 | P | 51326.871830 |
| 79 | 51797.529830   | 6        | 0.5 | 1.000000 | 9.39E-02  | 2.002186 | + | e | X | 32 | 0 | 0.5 | 0.5 | D | 51797.529830 |

Column Notation
1 n Energy level reference number (row)
2 $\tilde{E}$ Term value (in cm$^{-1}$)
3 $g_{rot}$ Total degeneracy
4 J Rotational quantum number
5 unc Uncertainty (in cm$^{-1}$)
6 $\tau$ Lifetime (s)
7 $g$ Landé factors
8 $+/−$ Total parity
9 $e/f$ Rotationless parity
10 State Electronic state
11 $v$ State vibrational quantum number
12 $\Lambda$ Projection of the electronic angular momentum
13 $\Sigma$ Projection of the electronic spin
14 $\Omega$ Projection of the total angular momentum ($\Omega = \Lambda + \Sigma$)
15 Source Source of term value; M = Marvel, P = Mollist (Brooke et al. 2014), D = Duo
16 $E_{\text{Duo}}$ Energy from Duo spectroscopic model

Figure 5. Dipole moment curves involving the three lowest electronic states of CN. The solid curves show the fitted Duo curves, the circles are ab initio calculations done in this work, and the crosses are the ab initio data from Mollist (Brooke et al. 2014) respectively, the experimental values are 1.45 ± 0.08 D and 1.15 ± 0.08 D (Thomson & Dalby 1968), similar to our equilibrium dipole moment of 1.34 D and 1.17 D.

3.3 Transitions file

The final line list contains 2,285,103 transitions, covering the wavenumber range 0-60,000 cm$^{-1}$. The transitions file is produced by combining the rovibronic wavefunctions produced by the energy spectroscopy model with the intensity spectroscopic model. Transitions were calculated for states with lower energies up to 30,000 cm$^{-1}$ as this contains 99 % of the total population at 5000 K. We have used a vibrational basis set up to $v = 120$ for each electronic state, and calculated rotational levels up to $J = 120.5$. Extracts of our final transitions files along with column descriptors are shown in Table 6.

Table 6. Extract from the transition file for $^{12}$C$^{14}$N. Full tables are available from www.exomol.com and in the Supporting Information.

| f  | i  | $A(f \leftarrow i)$ / s$^{-1}$ |
|----|----|-----------------------------|
| 181| 1  | 0.000010                    |
| 182| 1  | 3.080700                    |
| 183| 1  | 0.210810                    |
| 184| 1  | 0.002965                    |
| 185| 1  | 0.004063                    |

$f$: Upper (final) state counting number; $i$: Lower (initial) state counting number; $A(f \leftarrow i)$: Einstein $A$ coefficient in s$^{-1}$.
Figure 6. Cumulative density distribution of sources of energy levels in transitions across intensity, i.e. at each vertical slice, all transitions with intensities at or above the intensity at that x axis point are considered.

comparison the original MOLLIST line list includes 22,044 experimental transitions.

Figure 6 provides a more in-depth analysis by visually quantifying the source of the Trihybrid transition wavenumbers as a function of the cumulative transition intensity at 1000 K. Fully Marvel-ised transitions dominate in all intensity windows above $10^{-25}$ cm$^2$/molecule.

3.4 Isotopologues

Full spectroscopic models and line list have been generated for three isotopologues of CN ($^{13}$C$^{14}$N, $^{12}$C$^{15}$N, and $^{13}$C$^{15}$N), and the states and trans file have been included in the supplementary information. The states files for these isotopologues have been pseudo-hybridised, as is standard for ExoMol isotopologue models (Polyansky et al. 2017), by shifting the energy levels of the isotopologues by the deviation between the main isotopologue Duo and Marvel or MOLLIST energy, i.e. $E_{\text{isew}} = E_{\text{Duo}} + (E_{\text{main}} - E_{\text{Duo}})$ MOLLIST computed line lists for $^{13}$C$^{14}$N, $^{12}$C$^{15}$N are also available from Sneden et al. (2014).

3.5 Results and Discussion

3.5.1 Partition function

The partition function for CN was calculated using ExoCross (Yurchenko et al. 2018) across 10-7000 K in steps of 10 K using the following equation:

$$Q(T) = \sum_n g_{\text{tot}}^n \exp\left(-c_2 E_n / T\right),$$

where $g_{\text{tot}}^n$ is total degeneracy, $g_{\text{tot}}^n = g_n^{\text{ns}}(2J_n + 1)$, and $g_n^{\text{ns}}$ is the ‘physics’ interpretation of the nuclear spin statistical weight factor (Pavlenko et al. 2020), $c_2 = \hbar c / k_B$ is the second radiation constant (cm K), $E_i = E_i / \hbar c$ are the energy term values (cm$^{-1}$), taken from the states file, and $T$ is the temperature in K.

We compare our partition function to that of Sauval and Tatum (Sauval & Tatum 1984), Barklem and Collet (Barklem & Collet 2016), and the MOLLIST line list, as shown in figure 7. To make a direct comparison between our partition functions and those from Sauval & Tatum and Barklem & Collet we have multiplied their values by the nuclear spin statistical weight for CN, $g_{\text{ns}}^n = 3$ to be in the ‘physics’ convention which is used by ExoMol. All four partition functions show a strong agreement with a maximum relative deviation from the Trihybrid partition function of 0.16 from Barklem & Collet at 10,000 K.

3.5.2 Cross sections

Overview We computed the absorption cross-section at temperatures of 300 K, 1000 K, 3000 K, and 5000 K using a gaussian line profile with a half width half maximum (HWHM) of 2 cm$^{-1}$ in ExoCross, shown in figure 8. The spectra get less defined with the increase in temperature, as expected. Above 35,000 cm$^{-1}$ we see a very broadened cross section, losing almost all form at higher temperatures.

Decomposing the absorption cross section at 1000 K into
the bands in figure 9 we see a strong dominance across all wavenumbers from the \( A^2\Pi - X^2\Sigma^+ \) band. The \( X^2\Sigma^+ - X^2\Sigma^+ \) band sees a strong occurrence in the microwave region before dropping off significantly, while the \( B^2\Sigma^+ - X^2\Sigma^+ \) bands is very diminished at lower frequencies, but taking dominance above 25,000 cm\(^{-1}\). The strongest feature of the spectra has a cross sectional intensity up to \( 10^{-15} \) cm\(^2\) molecule\(^{-1}\) in the visible region, however there are strong (\( < 10^{-20} \) cm\(^2\) molecule\(^{-1}\)) peaks within the infrared, microwave, and ultraviolet regions as well.

**Comparison with the MOLLIST line list** In the first sub-figure of figure 10 we compare the full cross section of the MOLLIST line list and our hybrid line list from 0 - 60,000 cm\(^{-1}\) modelled at 1000 K with a HWHM of 2 cm\(^{-1}\) using ExoCross. We see the completeness that is gained from the DUO addition to the hybrid line list. The MOLLIST line list has a similar cross section, especially at lower wavenumbers, however decomposes with an increase in wavenumber. We can see the MOLLIST line list doesn’t extend much further than 50,000 cm\(^{-1}\), whereas the Trihybrid data extends much more smoothly out to 60,000 cm\(^{-1}\). The other panels of fig-
compare the MOLLIST cross sections and Trihybrid line list at a selection of key features. At wavenumber less than 4500 cm$^{-1}$ we can see that the MOLLIST line list does not contribute at all to the low frequency rotation lines, and while the Trihybrid does not include hyperfine transitions, it does still consider these rotational lines. The main infrared band is clearly matched well around 2000 cm$^{-1}$. The $A$ 2$\Pi$-X 2$\Sigma^+$ bands shown between 6600 and 18600 cm$^{-1}$ are also well matched. This is highlighted when we consider the main $A$ 2$\Pi$-X 2$\Sigma^+$ (0,0) band around 9000 cm$^{-1}$ with peak positions and intensities matching extremely well. We begin to see some more obvious discrepancies between MOLLIST and Trihybrid at higher energy. The main feature of the spectra (the $B$ 2$\Sigma^+$ - X 2$\Sigma^+$ band) is matched pretty well at 25750 cm$^{-1}$ but deviates above 27800 cm$^{-1}$ due to the lower number of rotational energy levels included in the MOLLIST line list. Additional comparisons are provided in the Supporting Information.

### 3.5.3 Rotational Spectroscopy

Our new trihybrid model contains the rotational transition data for all lower states with energies less than 30,000 cm$^{-1}$, thus comprehensively incorporating all rotational hot bands; recall that the MOLLIST data had no rotational transitions. However, for applications within microwave astronomy that focus on detecting a small number of strong lines, the existing CDMS data (collation (Müller et al. 2001, 2005) sourced from Dixon & Woods (1977); Skatrud et al. (1983); Johnson et al. (1984); Klisch et al. (1995)) is likely preferable due to the incorporation of hyperfine splitting that cannot yet be included in a DUO spectroscopic model (though future updates plan to add this feature to the program). CDMS has data for rotational transitions originating in the $v = 0$ and $v = 1$ states and can thus predict the strongest intensity hot bands.

Averaging over hyperfine structure, our line positions and the CDMS values agree well with a RMSD of 0.002 cm$^{-1}$, while the agreement in the Einstein $A$ coefficients is good with a RMSD of 0.012 s$^{-1}$, reflecting the close agreement between the experimental dipole moment used by CDMS and the equilibrium value of the $X$ 2$\Sigma^+$ state diagonal dipole moment curve used in our calculations.

### 3.5.4 Lifetimes

As discussed in McKemmish (2021), comparison of theoretical and experimental state lifetimes provide one of the most practical ways to validate the quality of ab initio off-diagonal transition dipole moment curves and thus the predicted intensities for rovibrionic transitions. Therefore, in Table 7, we compare our calculated excited state lifetimes with existing experimental and theoretical values.

The $B$ 2$\Sigma^+$ state results in Table 7 are straightforward; our results are within experimental uncertainties with strong agreement with MOLLIST (i.e. Brooke et al. (2014)) and reasonable agreement with other theoretical results.

The $A$ 2$\Pi$ state results, however, are more concerning. Our results are in close agreement with MOLLIST and in reasonable agreement with other theoretical results. However, the two experimental results differ considerably (sometimes more than a factor of 2) from both each other and from all ab initio-derived results. New experimental measurements would be highly desirable to validate or dispute the theoretical lifetimes (and thus the underlying dipole moment curves and predicted transition intensities). Astronomical or laboratory comparisons of the relative transition intensities in the $A$ 2$\Pi$-X 2$\Sigma^+$ and $B$ 2$\Sigma^+$-X 2$\Sigma^+$ bands (perhaps near the 20,000 cm$^{-1}$ region where both bands have comparable intensity) could also provide evidence to resolve this theory-experimental discrepancy.

### 4 PROBE TO CONSTRAIN THE VARIATION OF THE PROTON-TO-ELECTRON MASS RATIO

CN was identified as a potentially promising molecular probe to constrain the variation of the proton-to-electron mass ratio in Syme et al. (2019). This paper found that diatomic molecules with low lying electronic states show a sizeable amount of enhanced sensitive transitions to a variation of the proton-to-electron mass ratio. CN was further isolated as a potential probe due to its abundance and chemical properties. CN is one of very few molecules that has been detected at high redshift ($z = 2.56$ and 3.9) (Riechers et al. 2007; Guélin et al. 2007) along with H$_2$, HCN, CO, HCO$^+$. The presence of CN at high redshift is significant when probing large time separation for constraining fundamental constants, such as the proton-to-electron mass ratio. A key driver of the construction of the spectroscopic model created in this work was to test the transitions of CN for their sensitivity and evaluate the efficacy of CN as a molecular probe.

#### 4.1 Methodology

In Syme et al. (2019); Syme & McKemmish (2020a), we simulated a variation in the proton-to-electron mass ratio in diatomic molecules using spectroscopic models. We calculated the sensitivity of the transitions, $K$, in these diatomic molecules by matching the transitions on their id number in each simulation and using equation 2 with the matched transition frequencies using

$$\Delta \nu / \nu = K \Delta \mu / \mu,$$

(2)

where $\Delta \nu / \nu = \nu_{\text{shifted}} - \nu_{\text{unshifted}}$ is the relative change in the transition frequencies, $K$ is the sensitivity coefficient, and $\Delta \mu / \mu$ is the fractional change in the proton-to-electron mass ratio, simulated by a shift in the molecular mass.

As mentioned in the paper, there was a possibility that the id for the transitions was changed in the simulations and possible errors and miscalculations could arise. This method has been refined by matching the QNs of the energy levels from the states files and not using the transition id to identify a match. By matching on the QNs of the energy level we can account for the ordering of the states to change by the shift in the molecular mass. We have thus amended our approach to instead use

$$K_{\mu}(i \rightarrow j) = \frac{E_j k_j - E_i k_i}{E_j - E_i},$$

(3)

where $E$ is the energy of the lower ($E_i$) and upper ($E_j$) energy.
levels of the transitions, and $k$ is the sensitivity coefficients of the lower ($k_i$) and upper ($k_j$) energy levels in a transition.

In the refinement of our method for calculating the sensitivity of transitions in diatomic molecules we found significant changes to the maximum sensitivity in some of the diatomic molecules investigated. While the conclusions we drew from our results in Syme et al. (2019) remain the same, individual molecules have new results. The most dramatic change in the results for a single molecule was SiH, with a change in maximum $\Delta K$ from $\approx 9$ to $\approx 900$.

We continue to use the terminology of ‘enhanced’ transitions to describe transitions with a sensitivity coefficient $|K| > 5$. Again we only consider transitions below the intensity cutoff of $I < 10^{-30}$ cm$^2$ molecule$^{-1}$ at 1000 K.

### 4.2 Results for CN

Similar to the results in Syme et al. (2019) we see, in figure 11, that the enhanced transitions of CN have low transition frequencies ($<1000$ cm$^{-1}$) and involve the ground electronic state, $X^2\Sigma^+$ and the first excited electronic state, $A^2\Pi$. We note here that while there are 731 enhanced transitions in CN, all have intensities below $10^{-26}$ cm$^2$ molecule$^{-1}$ at 1000 K, and the lowest energy level of the enhanced transitions is greater than 9000 cm$^{-1}$. These limiting factors suggest that the enhanced transitions in CN might not be observable in the astrophysical environments that are probed to test the variation of the proton-to-electron mass ratio.

Given the observation of CN extra-galactically, it is worth considering whether stronger transitions with more modest $K$ could be useful. Restricting our search to intensities greater than $10^{-20}$ cm$^2$ molecule$^{-1}$ at 1000 K, we find that UV/optical transitions with $K$ values from -0.53 to 0.30 are observed, an order of magnitude larger than sensitivities obtained with H$_2$ transitions. However, UV/optical transitions are yet to be observed extragalactically for CN. Rotational transitions that have been observed extragalactically all have the sensitivity of pure rotational transitions, i.e. -1, not useful for a search for proton-to-electron mass variation.

### 4.3 Other diatomic molecules

A key finding in Syme et al. (2019) was the relationship between the energy of the first allowed excited state and the maximum sensitivity possible of the transitions considered. Here we provide an update on this relationship, shown in figure 12 which has the addition of CN and the sensitivities calculated from the recently published spectroscopic model for CP (Qin et al. 2021). We can see that while some of the data in this figure is different to that of figure 7 of Syme et al. (2019) the relationship remains consistent.
Figure 11. Spread of sensitivity of transitions within CN across energy.

Figure 12. Relation between the energy difference of the ground electronic state and the first spin/symmetry allowed excited electronic state and the maximum $|\Delta K|$ with the new inclusions of CP, and CN.

4.4 Future directions

The refined method of calculating the sensitivity coefficients of transitions within molecules with the energy levels will allow us to scale up to larger molecules with reasonable computational cost. We look forward to taking advantage of this with future work into the sensitivity to a variation of the proton-to-electron mass ratio of transitions within polyatomic molecules.

5 CONCLUSIONS

The complete Trihybrid line list for CN can be found online at www.exomol.com and in the Supplementary Information in the ExoMol format. The line list contains 2,285,103 transitions between 28,004 energy levels from the 3 lowest electronic states ($X^2\Sigma^+, A^2\Pi$, and $B^2\Sigma^+$) of the main isotopologue of CN. The final states file combines energy levels from MARVEL, MOLLIST, and ExoMol methodologies to produce a highly accurate and highly complete line list suitable for the full range of astrophysical applications from molecule detection using high-resolution cross-correlation techniques to modelling atmospheres to high precision.

Of particular note is our method of constructing the states file that combines experimentally derived empirical energy levels, energy levels from model hamiltonians and from variationally determined energy levels to produce the most accurate states file. This is a good approach moving forward and we expect to see many future line lists utilising this approach of line list generation.

A key motivator of this work was the development of a spectroscopic model to evaluate the efficacy of CN as a molecular probe to constrain the variation of the proton-to-electron mass ratio. While the sensitivities of the transitions within CN are not particularly enhanced, we do see some potential for CN to be used as a molecular probe if UV/optical transitions can be detected as it is a common molecule in various astrophysical environments.

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The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data underlying this article are available in the article and in its online supplementary material. These include the following files;

- DUO spectroscopic model and input file (12C-14N__Trihybrid_Duomodel.inp)
- Trihybrid states file (12C-14N__Trihybrid.states)
- Trihybrid transitions file for $^{12}$C$^{14}$N (12C-14N__Trihybrid.trans)
- Partitian function up to 10,000 K for $^{12}$C$^{14}$N (12C-14N__Trihybrid.pf)
- Isotopologue states and transition files (in the isotopologue folder)
- A sample ab initio input file (multi_ci_SO_1.35.inp)
- csv file containing the PEC, TDM, and SOC from all of the $ab\ initio$ calculations (abinitio_results.csv)
- Updated MARVEL transitions and energy levels (12C-14N_MARVEL_2021update.txt and 12C-14N_MARVEL_2021update.energies respectively).

We note that the data generated in section 4 can be reproduced through the use of the CN spectroscopic model given here, as well as the available spectroscopic models on the ExoMol website (www.exomol.com), using the method described in the paper.
ADDITIONAL SUPPORTING INFORMATION

As well as the data files described above, we include as supporting information two additional figures and associated discussion comparing (a) the new trihybrid and existing MOLLIST line lists and (b) the new trihybrid line list created using the MOLLIST X-X, A-X and B-X dipole moment curves compared to the results when using our new smaller basis set result curves.

For clarity, all supporting information files are described in README_SI_CN_linelist.pdf.

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