Extending the Rotational Library of 1- and 2-Cyanocyclopentadiene: Millimeter-wave Transitions for Astronomical Searches in Hot Cores

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TMC-1: A Molecular Factory for Aromatic Nitriles

Cold dark cloud ($T \approx 10$ K) with unexpectedly rich cyclic and aromatic chemistry Cernicharo et al. 3, Loru et al. 9, McGuire et al. 12, Wenzel et al. 18

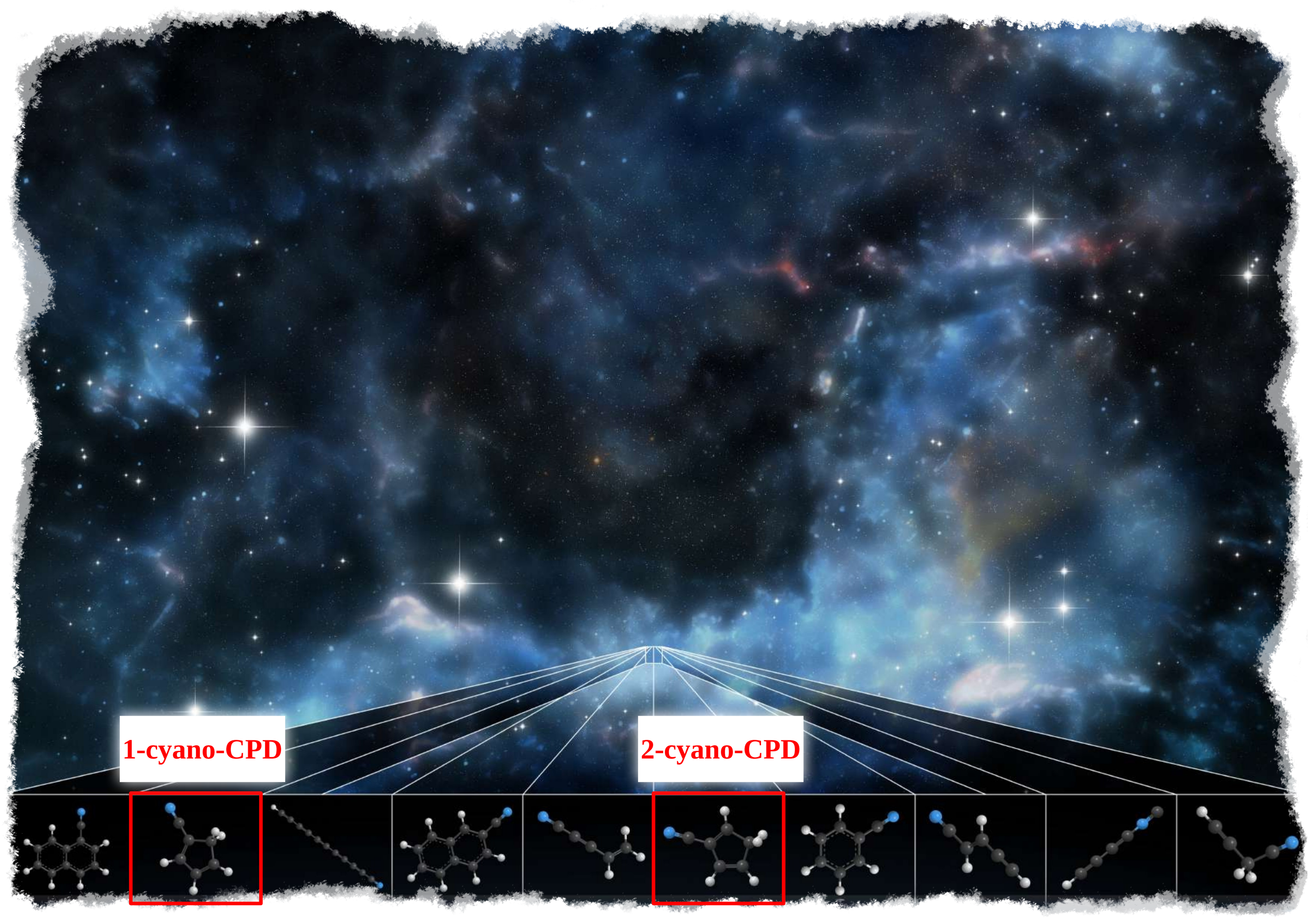


Figure 1. Detected molecules in TMC-1: M. Weiss / Center for Astrophysics | Harvard & Smithsonian

Why extend to millimeter waves?

- Existing data limited to cm-wave → large extrapolation errors at high frequencies [1, 15]
- Centrifugal distortion effects scale with J (up to 10^2-10^3 kHz drift)
- Hot cores require accurate mm/sub-mm catalogs for line identification [5, 8]
- Higher-order constants (sextic, octic) only accessible with high-J measurements

Molecular Structures: Two Cyclic Isomers

Chemical formula: C_6H_5N (five-membered ring with CN group)

1-cyano-CPD	2-cyano-CPD
(1-cyano-1,3-cyclopentadiene)	(2-cyano-1,3-cyclopentadiene)
Most stable	+5 kJ mol^{-1}
E = 0 kJ mol^{-1}	higher energy
$\kappa = -0.9010$ (near-prolate)	$\kappa = -0.8977$ (near-prolate)
$\mu_a = 4.15$ D [4, 17]	$\mu_a = 4.36$ D [17]
$\mu_b \approx 0$ D	$\mu_b \approx 0$ D

Both isomers detected in TMC-1 via GOTHAM survey [6, 11, 13]

Experimental Setup: FAST Spectrometer

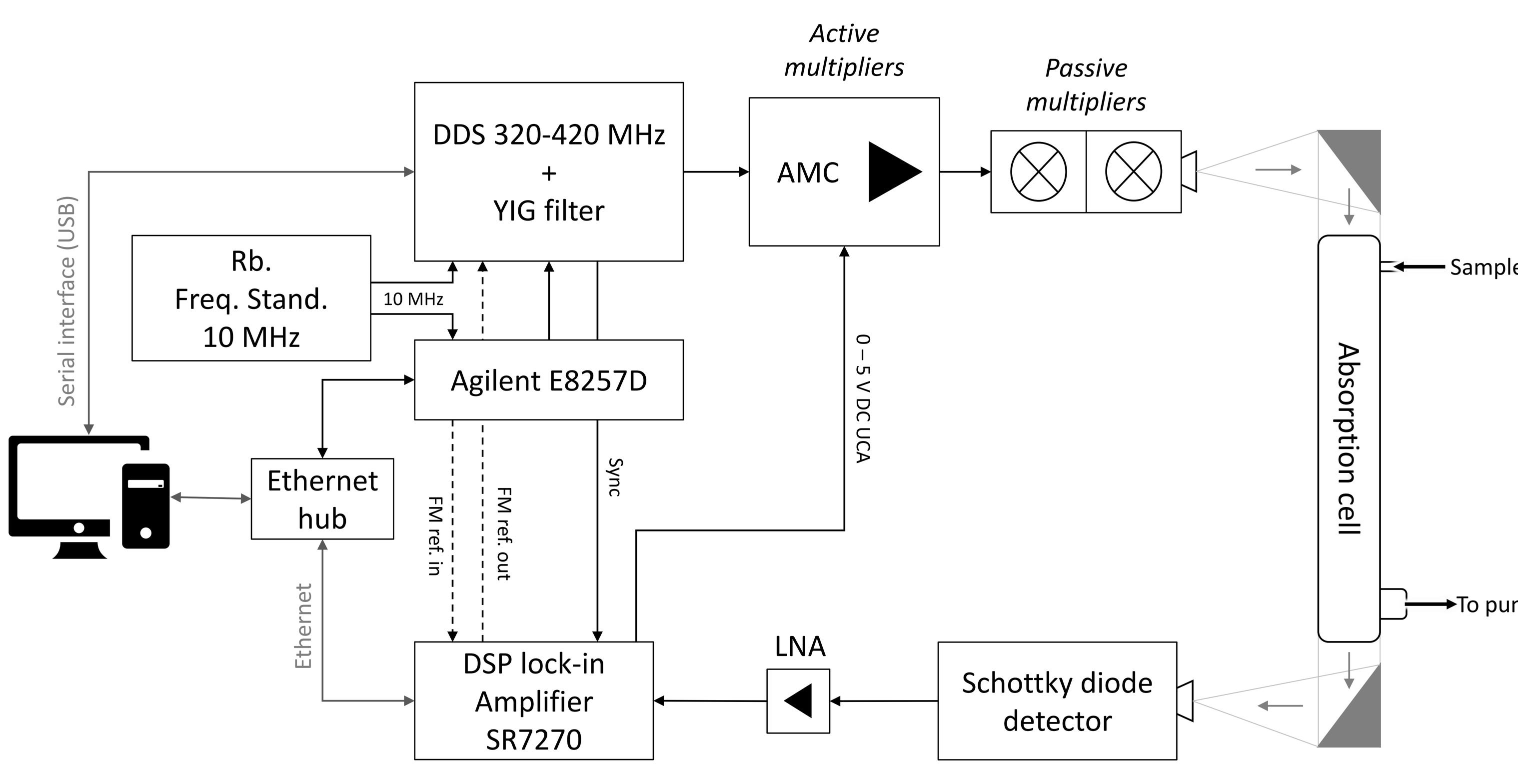


Figure 2. Lille Fast-scan absorption spectrometer (FLASH) [19]

Spectroscopic Results: Extended to 75–500 GHz

1-cyano-CPD	2-cyano-CPD
7,219 transitions	**4,075** transitions
$J_{max} = 153$, $Ka_{,max} = 50$	$J_{max} = 153$, $Ka_{,max} = 37$
RMS = **47.5 kHz**	RMS = **44.8 kHz**

- **33 spectral bands** recorded (5–15 GHz each)
- **12 new parameters** determined (sextic + octic terms) using ASFIT [7]
- **10× improvement** in rotational constants
- **1000× improvement** in quartic centrifugal distortion
- Only a-type R-branches fitted (μ_a-dominated)
- Catalogs generated with SPFIT/SPCAT [14]

Rotational Constants: Watson A-reduction, I^r

Comparison of the number of significant digits determined in this work versus previous studies. The higher precision (more significant digits) in rotational constants and distortion parameters is crucial for accurate extrapolation to the mm/sub-mm domain [16].

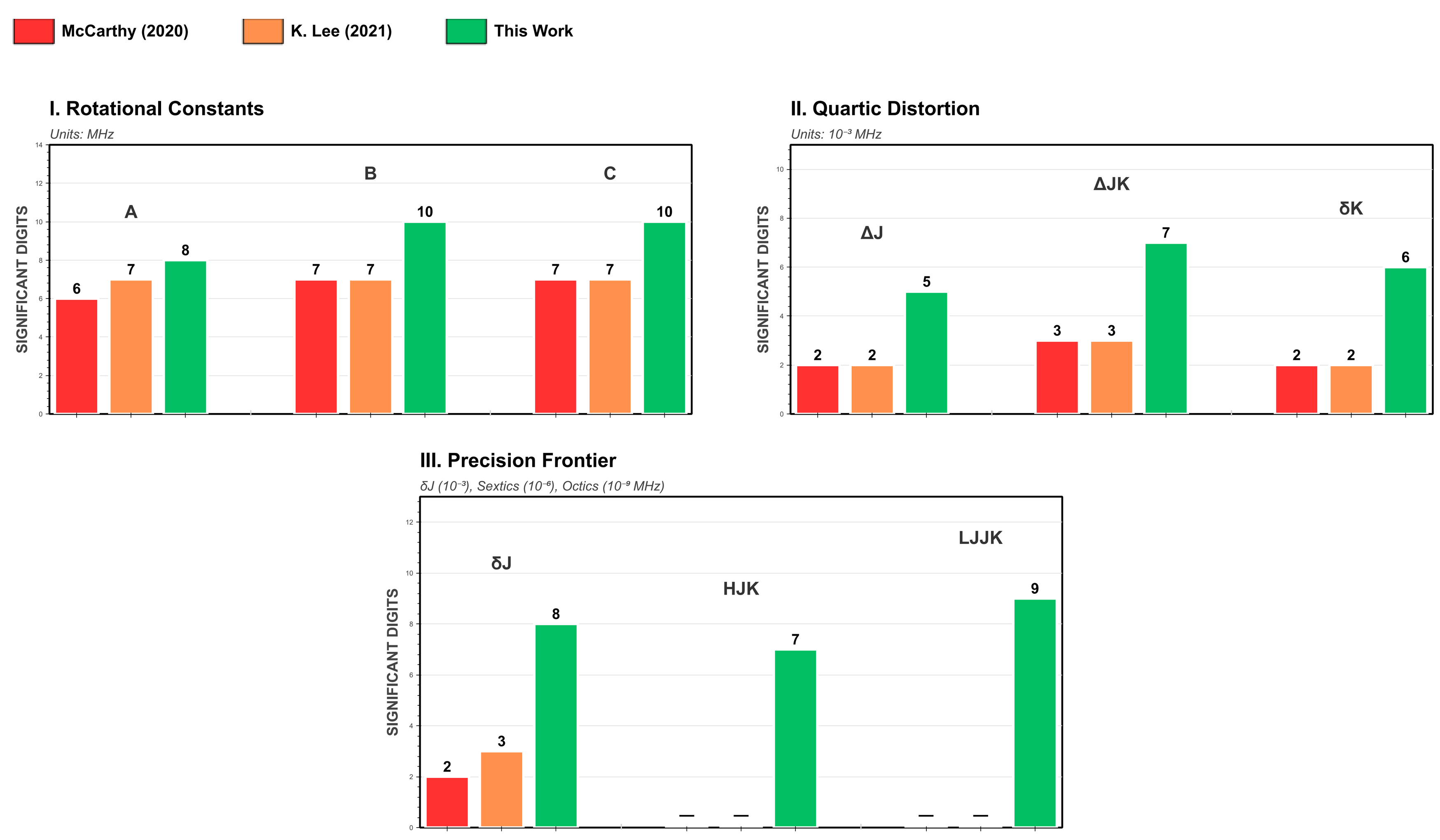
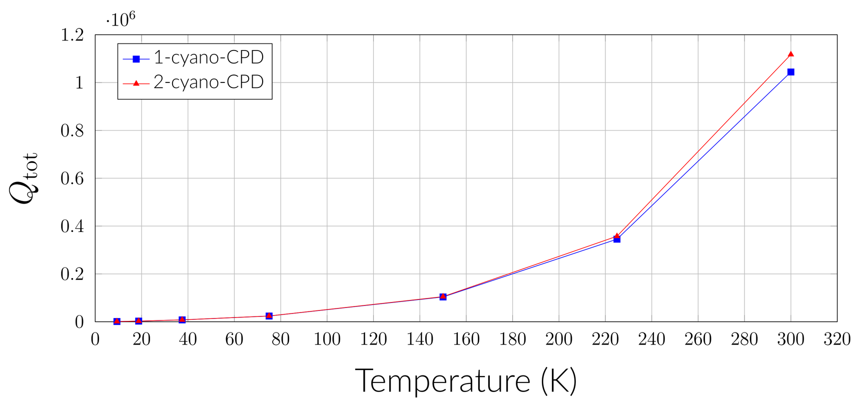


Figure 3. Significant digits comparison. Colors: McCarthy (2020), Lee (2021), This Work. Extension to higher frequencies allows determining higher order parameters (sextics, octics).

Partition Functions: Critical for Hot Core Searches

Precise partition function calculations are essential for accurate column density determinations in warm interstellar regions [16].



Key Temperatures:

T (K)	Q_{rot}	Q_{vib}	Q_{tot}
75	22K	1.09	24K
150	62K	1.67	104K
225	114K	3.03	345K
300	**175K**	**5.95**	**1.04M**

Critical Finding:

- At 300 K, Q_{vib} contributes **6× factor**
- Neglecting vibrational states → major column density underestimation [16]
- Essential for hot core LTE modeling

Astronomical Search in Hot Interstellar Medium

Objective: Extend TMC-1 detections to warmer environments [10]

LTE Modeling:

- Single temperature assumption
- Optically thin regime
- Column density determination
- Suitable for compact hot cores

Non-LTE Modeling:

- Collisional rates required
- Density/temperature gradients
- Line intensity ratios
- More accurate for extended regions

Challenges in Hot Cores:

- **Line confusion:** Crowded spectral regions require precise frequencies [16]
- **High opacity:** Multiple species overlapping in mm/sub-mm bands
- **Excitation:** Vibrational states populated at $T > 100$ K

Status

Frequency catalogs generated · Search methodology established · **Ongoing analysis**

Key Findings Impact

Spectroscopic Achievements:

- ✓ Extended to **75–500 GHz**
- ✓ **11,294 transitions** assigned
- ✓ **12 new parameters** determined
- ✓ **10×** precision improvement

Astronomical Impact:

- ✓ Accurate mm/sub-mm catalogs
- ✓ Partition functions to 300 K
- ✓ Ready for hot core searches
- ✓ Reduces line confusion [16]

These high-precision catalogs enable robust identification of cyclic nitriles in crowded hot core spectra, supporting studies of PAH formation pathways in warm interstellar environments [2, 10].

References

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