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Laboratory Detection of Cyanoacetic Acid: A Jet-Cooled Rotational Study

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Abstract

Herein we present a laboratory rotational study of cyanoacetic acid ($\text{CH}_2(\text{CN})\text{C}(\text{O})\text{OH}$), an organic acid as well as a $-\text{CN}$ bearing molecule, that is a candidate molecular system to be detected in the interstellar medium (ISM). Our investigation aims to provide direct experimental frequencies of cyanoacetic acid to guide its eventual astronomical search in low-frequency surveys. Using different jet-cooled rotational spectroscopic techniques in the time domain, we have determined a precise set of the relevant rotational spectroscopic constants, including the ^{14}N nuclear quadrupole coupling constants for the two distinct structures, *cis*- and *gauche*-cyanoacetic acid. We believe this work will potentially allow the detection of cyanoacetic acid in the interstellar medium, whose rotational features have remained unknown until now.

Keywords

catalogs; ISM: molecules; molecular data; techniques: spectroscopic

1 Introduction

Laboratory astrophysics plays a crucial role in understanding our molecular universe by supplementing astronomical searches and assisting astrochemists in building up theoretical models (Savin et al., 2012, Tielens 2013). The field of laboratory astrophysics embraces several areas of physics relevant to astronomy and astrophysics. Among them, the symbiotic relationship between radioastronomy and laboratory rotational studies has enabled the detection of many interstellar molecules (Herbst & van Dishoeck 2009). In current astrophysical research, a battery of state-of-the-art rotational spectroscopic techniques in

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the frequency and time domain has been devoted to investigating elusive solid compounds of astrophysical interest in the isolation conditions of the gas phase. Many organic compounds with relatively high melting points usually exhibit very low vapor pressure, being sometimes out of the scope of conventional gas-phase microwave and millimeter-wave studies. Thus, besides conventional heating methods (Sanz-Novo et al. 2020 (a)), we have coupled laser ablation sources with high-resolution Fourier transform microwave techniques to characterize most of the coded amino acids (Alonso et al. 2015, Alonso et al. 2021). Other species of astrophysical relevance such as hydantoin (Alonso et al. 2017), hydantoic acid (Kolesníková et al. 2019), glycinamide ($\text{CH}_2(\text{NH}_2)\text{C}(\text{O})\text{NH}_2$) (Alonso et al. 2018), and cyanoacetamide ($\text{CH}_2(\text{CN})\text{C}(\text{O})\text{NH}_2$) (Sanz-Novo et al. 2020 (b)) have been recently reported.

Organic acids constitute much of the required material a planet needs to support life. These compounds belong to an influential group of molecules entitled interstellar Complex Organic Molecules (iCOMs, Herbst & van Dishoeck 2009, Ceccarelli et al. 2017). These molecules have received increasing attention in the last decade since they are essential to unveil how chemical complexity builds up. The simplest forms of these molecular classifications, formic acid ($\text{HC}(\text{O})\text{OH}$) and acetic acid ($\text{CH}_3\text{C}(\text{O})\text{OH}$) are well-known interstellar molecules (Liu et al. 2002; Lefloch et al. 2017; Favre et al. 2018; Remijan et al. 2003 and Jørgensen et al. 2016). Among all iCOMs, cyano-bearing compounds, organic molecules containing a cyano functional group ($-\text{CN}$), are among the most widely distributed and best-known species in the ISM. In the early 40's, the diatomic cyano radical, CN , was the second molecule to be identified in the ISM (McKellar 1940). CN 's first rotational transition ($J = 1 \leftarrow 0$) was detected 30 years later in the Orion Nebula and W_{51} (Jefferts et al. 1970). Since then, more than 30 complex cyanide species have been found in diverse types of astronomical environments, including the detection of the branched *i*-propyl cyanide ($i\text{-C}_3\text{H}_7\text{CN}$) (Belloche et al. 2014), glycolonitrile ($\text{HO-CH}_2\text{-CN}$) (Zeng et al. 2019), benzonitrile ($c\text{-C}_6\text{H}_5\text{CN}$), the first benzene-derived aromatic molecule in the ISM (McGuire et al. 2018) and cyanocyclopentadiene, its five-membered ring analog (McCarthy et al. 2021). Also, very recently, several $-\text{CN}$ and $-\text{NC}$ bearing molecules, highlighting HC_4NC , HCCH_2CN , HC_5NH^+ , $\text{H}_2\text{CCHC}_3\text{N}$, and HCCCHCHCN , have been detected towards the prototypical cold dark molecular cloud TMC-1 (Cernicharo et al. 2020, McGuire et al. 2020, Marcelino et al. 2020 and Lee et al. 2021). However, many simple cyanides have yet to be discovered. Consequently, new experimental studies exploring related species should represent an essential source of reference data in constraining models on the formation of $-\text{CN}$ and $-\text{C}(\text{O})\text{OH}$ bearing molecules in the ISM and predicting which other iCOMs might be lurking in the expanses of space.

Following our previous work, we have performed state-of-the-art experiments to achieve the first rotational characterization of cyanoacetic acid ($\text{CH}_2(\text{CN})\text{C}(\text{O})\text{OH}$), a $-\text{CN}$ bearing organic acid as a candidate for interstellar detection. Only IR and FTIR-matrix studies have been reported so far (Binev et al. 1998 and Reva et al. 2003 (a, b)) and, to the best of our knowledge, no rotational spectroscopic data is available for cyanoacetic acid. Our current study aims to provide accurate experimental rotational information, which is the initial and prerequisite step for its radio astronomical search, to correctly reproduce the spectrum and interpret astronomical data in low-frequency regions.

2 Jet-Cooled Rotational Spectrum

Concurrent to the laboratory work and to guide the spectral search, we performed high-level computations on the conformational panorama of cyanoacetic acid complementing those of Reva et al. 2003 (a, b). We employed a double-hybrid density functional (B2PLYPD3), which includes non-local electron correlation effects (Schwabe & Grimme 2007) and the augmented correlation-consistent polarized valence triple- ζ , (aug-cc-pVTZ) basis set (Dunning 1989; Woon & Dunning 1993). Two predominant conformers (labeled as *cis* and *gauche*) were found, differing in the values of the CCC=O dihedral angle of the molecule (see Figure 1). We theoretically explored the plausible relaxation pathways from *cis*- to *gauche*- cyanoacetic acid and found a barrier of 275 cm^{-1} (3.3 kJ/mol) at the B2PLYPD3/aug-cc-pVTZ level. The predicted spectroscopic constants are collected in Table 1.

Briefly, we have transferred neutral molecules of cyanoacetic acid to the gas phase using a multi-nozzle heated system and probed them with a chirped pulse Fourier transform microwave spectrometer (CP-FTMW) (Mata et al. 2012). In this experiment, cyanoacetic acid was conventionally heated at $70\text{ }^{\circ}\text{C}$. It was seeded in Helium to minimize plausible interconversion between the *gauche*- and *cis*- forms (Ruoff et al. 1990; Godfrey et al. 1996) (backing pressure of 1 bar) and adiabatically expanded into the vacuum chamber of the spectrometer to generate a supersonic-jet. We employed a 300 W microwave excitation pulse to polarize the molecules macroscopically and collected 57,000 individual free induction decay signals (four FIDs per cycle) in the time domain. These were subsequently Fourier-transformed to obtain the broadband spectrum in the frequency domain.

The broadband rotational spectrum measured for cyanoacetic acid from 8 to 18 GHz is presented in Figure 2 (a). Strong water dimer (H_2O)₂ signals and other lines belonging to decomposition products were quickly spotted and rejected from the analysis in a first step. At first glance, we quickly recognized an intense $^a\text{R-branch } (J+1)_{0,J+1} \leftarrow J_{0,J}$ progression ascribable to a first rotamer, labeled as I. We further extended the initial assignment to *b*-type rotational transitions (with *J* ranging from 0 to 5). All transitions were observed split into various hyperfine components due to the ^{14}N nuclear quadrupole coupling interactions. However, the resolution reached with our broadband CP-FTMW technique was not enough to completely resolve the hyperfine patterns (see Figure 2(b)). In a first step, no attempt was performed to analyze the ^{14}N nuclear hyperfine structure, but rather the intensity-weighted mean of the hyperfine line cluster was measured and fitted (Pickett 1991) to a rigid rotor Hamiltonian to give the first set of rotational constants ($A = 10191.3$, $B = 2267.2$ and $C = 1877.3$) (in MHz) for rotamer I. As shown in Table 1, they perfectly match those theoretically predicted for the *cis*- form.

Once all the lines corresponding to *cis*- form were discarded from the analysis, we discovered a new weaker progression of $^a\text{R-branch}$ transitions, attributed to another rotamer, labeled as II. We further confirmed the assignment by predicting and measuring additional *a*-type lines. However, *b*- and *c*-type lines were predicted but not observed. We obtained an initial set of rotational constants for rotamer II ($A = 9278.6$, $B = 2357.8$ and $C = 1966.7$) (in MHz), which nicely agrees with those calculated for the *gauche*- form (see Table 1).

Surprisingly, after excluding all the spectral signatures corresponding to both *cis*- and *gauche*- conformers, a small number of rotational lines remained unassigned. These lines most probably belong to the cyanoacetic acid monohydrate founded on the observation of strong water dimer (H₂O)₂ rotational transitions due to residual water. In this context, we managed to recognize a set of *a*-type *R*-branch transitions (spaced approximately by $B + C$) corresponding to a cyanoacetic acid-water rotamer [see Fig. 2 (a)]. We performed detailed searches for *b*- and *c*- type transitions, but they were not observed. Rotational constants and planar moments of inertia are collected in Table 2, while the complete list of measured transitions is provided in Table A1 in de Appendix. The structure of the cyanoacetic acid-water cluster is unambiguously confirmed by a comparison of the experimental and B2PLYPD3 predicted rotational parameters (see Table 2), showing that the observed rotational constants are in good agreement with those calculated for the global minimum (*w-cis* cyanoacetic acid in Figure 1 (b)). Moreover, the value of the planar moment (1.9162 uÅ²) is very similar to that of the *cis*- monomer (1.6434 uÅ²). It further suggests a nearly planar configuration, with the skeleton framework lying on the *ab* inertial plane, and only the water hydrogen's out-of-plane contributions corroborate the assignment. Although the monohydrated form itself is not expected to be a candidate for interstellar detection, this precise spectroscopic information should be helpful in future theoretical studies as a reference point in the characterization of plausible gas and gas-grain mechanisms involving cyanoacetic acid and water in the context of the ISM.

3 ¹⁴N Hyperfine Nuclear Quadrupole Coupling: Narrowband Rotational Spectrum

A more challenging endeavor was the resolution of the nuclear quadrupole hyperfine structure. For observations in cold and quiescent molecular clouds such as TMC-1, the hyperfine structure could be a key issue for decoding the radioastronomical spectra (McCarthy & McGuire 2021). For instance, the interpretation of the hyperfine patterns of several interstellar molecules, such as cyanoallene (Lovas et al. 2006) and benzonitrile (McGuire et al. 2018), was crucial for their conclusive identification in the ISM. Hence, we profit from the subdoppler resolution of our narrowband MB-FTMW spectrometer (Balle & Flygare 1981; Alonso et al. 1997) to resolve the hyperfine structure. The analysis began with measuring five hyperfine components of the 20₂ ← 1_{0,1} transition belonging to *cis*-cyanoacetic acid and was further extended to other *a*- and *b*- type *R*-branch transitions. Once the analysis was completed, new $K=1 \leftarrow 0^a$ *R*-branch transitions attributable to the *gauche*-form were identified. In this case, the MB-FTMW spectrometer's resolution was mandatory to unravel the ¹⁴N nuclear quadrupole structure (see Figure 2 (c)).

In a further step, we employed our double-resonance configuration (described in Sanz-Novo et al. 2020 (b)), with which hyperfine components can be resolved, seeking an extension of our measurements to higher frequencies. We focused our attention on the most stable form, *cis*- cyanoacetic acid. We measured a total of 90 hyperfine components (together with the previous CP-FTMW and MB-FTMW measurements correctly weighted). We fitted them (Pickett 1991) using the *A*-reduction Hamiltonian in the *I*^r representation (H_R^(A)) (Watson 1977), complemented with an additional term that accounts for the nuclear quadrupole

coupling effects (HQ) (Foley 1947; Robinson & Cornwell 1953), ($H = H_A^{(A)} + H_Q$). The rotational Hamiltonian was set up in the coupled basis set $F = J + I$ to describe the energy levels of the hyperfine structure in terms of the quantum numbers J , K_a , K_c , and F . We list the final set of spectroscopic parameters for *cis*- and *gauche*-cyanoacetic acid in the first and third column of Table 1, respectively. A sample list of the measured transitions for the *cis*-form is reported in Table 3. All measured lines for both rotamers are provided in Tables A2–A3 in the Appendix. We detected an unusual nonrigid behavior for the *gauche*-form reflected in large values of the J and JK centrifugal distortion constants compared to those obtained for the *cis*-form. This behavior can be ascribed to a large amplitude motion regarding the CCCO bond torsion, resulting in a double minimum potential function with a low-energy barrier at the planar skeleton framework. The potential energy surface scan of the $\angle\text{CCCO}$ torsion confirmed the presence of such a double minimum, separated by a barrier of 25 cm^{-1} (0.3 kJ/mol), which is similar to that observed for glycineamide (Alonso et al. 2018). As shown in Figure 3, two isoenergetic forms are separated by a torsion barrier that is low enough to split the ground state into two close-lying states (0^+ and 0^-). Only the lowest-lying 0^+ state is observed due to vibrational cooling. This fact helps us to rationalize the requirement of rather large centrifugal distortional parameters for low J values and, therefore, explain the conformer's unexpected nonrigid nature.

All in all, the microwave spectrum of cyanoacetic acid has been explored up to 40 GHz to provide precise laboratory reference spectra that are needed to compare directly against low-frequency observational data in different regions of the ISM. With our measurements, cyanoacetic acid's rotational transitions can be predicted with linewidths (FWHM) of about 0.1 km s^{-1} up to 40 GHz in equivalent radial velocity. It is more than enough for a radioastronomical search in the dark, cold molecular clouds, where lines with very narrow linewidths are expected ($0.3\text{--}0.4\text{ km s}^{-1}$) (McCarthy et al. 2021). In conclusion, this high-resolution spectroscopic information can be confidently used in future searches for cyanoacetic acid in various low-frequency surveys, such as the Green Bank Observatory (GBT) surveys (McCarthy et al. 2021) and the Effelsberg 100-m (Sanz-Novo et al. 2020 (b)) and Yebes 40-m observations (Cernicharo et al. 2021).

Finally, in Table 4 we list the rotational (Q_r) and vibrational (Q_v) partition functions of cyanoacetic acid. We calculated Q_r 's values from first principles across the standard temperatures by SPCAT (Pickett 1991) as implemented in the JPL database (Pickett et al. 1998). We performed double-hybrid calculations at the B2PLYPD3/aug-cc-pVTZ level of theory to obtain the expected normal frequency modes (see Table A3). Afterward, we predicted the vibrational part, Q_v , using a harmonic approximation and a simple formula that coincides with Eq. (3.60) of Gordy & Cook (1970). The vibrational contributions were calculated by considering the lowest vibrational modes up to 1000 cm^{-1} . The total partition function, Q_{tot} , is, therefore, the product of Q_r and Q_v , and does not include the hyperfine structure.

4 Conclusions

There is good reason to expect many astronomical discoveries given improvements in laboratory instrumentation and techniques and the construction of radio telescopes with

unprecedented sensitivity regimes, remarking those directed towards low-frequency regions. A thoroughly coordinated laboratory, modeling and observational effort will be essential to understand the origin and evolution of more complex –CN and -C(O)OH bearing systems. In this context, we have investigated the rotational spectrum of cyanoacetic acid in the microwave region. The capability of jet-cooled experiments coupled with time-domain Fourier transform microwave spectroscopy has enabled the first high-resolution rotational characterization of this elusive molecule. For both *cis*- and *gauche*- forms, precise experimental values of the rotational constants, the ^{14}N nuclear quadrupole coupling constants, and the quartic centrifugal distortion constants are determined to reproduce the spectrum. The ^{14}N hyperfine structure acts as a fingerprint probe in the molecular identification in the low-frequency surveys, increasing the power of these jet-cooled spectroscopic techniques in molecular astrophysics.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
a) Structures of the cyanoacetic acid monomers: *cis*- (left) and *gauche*-cyanoacetic acid (right) showing the ^{14}N nucleus; b) Structure of the water cluster: *w-cis* cyanoacetic acid.

Figure 2.

a) Jet-cooled broadband rotational spectrum of cyanoacetic acid from 8 to 18 GHz. b) Zoom-in view of the spectrum showing the $2_{0,2} \leftarrow 1_{0,1}$ transition of rotamer II (*gauche*-cyanoacetic acid) with unresolved ^{14}N hyperfine structure; c) Completely resolved hyperfine pattern of the same transition attained with the cavity-based MB-FTMW technique. The intensity is given in arbitrary units.

Figure 3. Relaxed potential energy surface (PES) scan computed at the B2PLYPD3/aug-cc-pVTZ level, choosing the $\angle$ CCCO torsion as the driving coordinate. A torsion barrier of 0.3 kJ/mol (25 cm^{-1}) connects the two isoenergetic *gauche*- forms.

Table 1
Theoretical and final set of experimental spectroscopic parameters of cyanoacetic acid.

Parameters	Rotamer I	Rotamer II	<i>cis</i> ^[a]	<i>gauche</i>
A [h] / MHz	10191.2722 (19)	9255.1 (12)	10199.5	9200.8
B / MHz	2267.21502 (58)	2357.7873 (10)	2262.7	2352.4
C / MHz	1877.26749 (44)	1966.7410 (10)	1873.0	1967.6
J / kHz	0.344 (18)	3.771 (77)	0.434	1.345
JK / kHz	2.184 (86)	23.9 (13)	2.223	10.59
K / kHz	9.57 (64)	-	7.754	220.6
δJ / kHz	0.0776 (45)	-	0.0867	31.03
P_c [c]	1.6435 (10)	5.983 (13)	1.539	6.456
$ \mu_a , \mu_b , \mu_c $ [d]	Yes / Yes / No	Yes / No / No	3.9 / 2.9 / 0.0	2.1 / 0.5 / 1.3
$^{14}\text{N } \chi_{aa}$ [e]	-3.2108 (32)	-2.8203 (46)	-3.379	-2.937
$^{14}\text{N } \chi_{bb} - \chi_{cc}$	-0.9058 (76)	-0.692 (14)	-0.951	-0.637
$^{14}\text{N } X_{ab} $	2.271 (91)	-	2.564	2.474
N [f]	90	25	-	-
σ [g]	13.0	3.3	-	-
E_{TOTAL} [h]	-	-	0.0	49.3

[a] Theoretical computations at the B2PLYPD3/aug-cc-pVTZ level.

[b] A , B , and C are the rotational constants (in MHz);

[c] P_c is the planar moment of inertia (in $\text{u}\text{\AA}^2$), conversion factor: $505379.1 \text{ MHz}\cdot\text{u}\text{\AA}^2$.

[d] μ_a , μ_b , and μ_c are the electric dipole moment components (in D).

[e] χ_{aa} , χ_{bb} and χ_{cc} represent the diagonal elements of the ^{14}N nuclear quadrupole coupling tensor (in MHz);

[f] N is the number of measured hyperfine components.

[g] σ is the root mean square (rms) deviation of the fit (in kHz).

[h] E_{TOTAL} is the electronic and Gibbs free energies (in cm^{-1}) at 298 K relative to the global minimum calculated at the B2PLYPD3/aug-cc-pVTZ level of theory, taking into account the zero-point vibrational energy (ZPE) for the electronic energy ($E_{\text{TOTAL}} = E + E_{\text{ZPE}}$) calculated at the same level. [i] Standard error in parentheses in units of the last digit.

Table 2
Predicted and experimental spectroscopic parameters for the cyanoacetic acid-water cluster.

Parameters	rotamer w-I	w-cis ^[a]
A ^[b] / MHz	7074.50 (33) ^[h]	7116.6
B / MHz	1158.6515 (11)	1169.8
C / MHz	1003.1681 (13)	1012.7
J / kHz	0.204 (9)	-
J_K / kHz	-4.68 (21)	-
P_c ^[c]	1.9162 (11)	1.997
$ \mu_a , \mu_b , \mu_c $ ^[d]	Yes / No / No	3.5 / 2.4 / 1.0
N ^[e]	14	-
σ ^[f]	15.2	-
E_{TOTAL} ^[g]	-	0.0

^[a] Theoretical computations at the B2PLYPD3/aug-cc-pVTZ level of theory.

^[b] A , B , and C represent the rotational constants (in MHz);

^[c] P_c is the planar inertial moment (in uÅ²), conversion factor: 5 05379.1 MHz-uÅ².

^[d] μ_a , μ_b , and μ_c are the electric dipole moment components (in D);

^[e] N is the number of measured transitions.

^[f] σ is the root mean square (rms) deviation of the fit (in kHz).

^[g] E_{TOTAL} is the electronic energy (in cm⁻¹) relative to the global minimum calculated at the B2PLYPD3/aug-c-pVTZ level of theory, taking into account the zero-point vibrational energy (ZPE) for the electronic energy $^3\text{ }^{14}\text{N}$ ($E_{TOTAL} = E + E_{ZPE}$) calculated at the same level

^[h] HYPERFINE Standard error in parentheses in units of the last NUCLEAR digit.

Table 3
Sample list of the measured transition frequencies for the ground-state of cyanoacetic acid.

Technique	J'	K _a '	K _c '	F'	J''	K _a ''	K _c ''	F''	U _{obs} ^a (MHz)	U _{calc} ^b (MHz)	U _{obs} -U _{calc} ^c (MHz)
MB-FTMW	2	1	2	2	1	1	1	1	7898.1967	7898.1967	0.0001
	2	1	2	2	1	1	1	2	7898.5439	7898.5424	0.0015
	2	1	2	3	1	1	1	2	7899.2045	7899.2039	0.0006
	2	1	2	1	1	1	1	2	7899.5725	7899.5717	0.0007
	2	1	2	1	1	1	1	0	7900.0909	7900.0901	0.0008
	3	1	2	3	2	1	1	2	13009.1663	13009.1648	0.0015
	3	1	2	4	2	1	1	3	13009.4489	13009.4480	0.0009
	3	1	2	2	2	1	1	1	13009.4668	13009.4709	-0.0041
CP-FTMW	2	1	2	1	1	0	1	0	15821.9328	15821.9533	-0.0205
	2	1	2	2	1	0	1	2	15822.3606	15822.3688	-0.0081
	2	1	2	3	1	0	1	2	15823.0169	15823.0303	0.0133
	2	1	2	2	1	0	1	1	15823.3103	15823.3319	-0.0216
	2	1	2	1	1	0	1	1	15824.3454	15824.3613	-0.0159
DR-MB-FTMW	5	1	5	5	4	0	4	4	26032.0800	26032.0715	0.0085
	5	1	5	6	4	0	4	5	26032.1200	26032.1139	0.0061
	2	2	0	1	1	1	1	0	32854.6280	32854.6368	-0.0088
	2	2	0	3	1	1	1	2	32854.6940	32854.6951	0.0011
	2	2	0	2	1	1	1	1	32854.7600	32863.7728	0.0138

Notes. Upper and lower state quantum numbers are indicated by ' and'', respectively.

^(a) Observed frequency.

^(b) Calculated frequency.

^(c) Observed minus calculated frequency.

Table 4
Rotational and vibrational partition functions of *cis*- cyanoacetic acid.

Temperature (K)	$Q_r^{(a)}$	$Q_v^{(b)}$
3.00	134.3515	1.0001
9.38	737.1679	1.0008
18.37	2081.8097	1.0293
37.50	5884.2420	1.2065
75.00	16640.5107	1.7985
150.00	47079.8270	3.9574
225.00	86551.9930	8.7615
300.00	133184.4558	19.5677

Notes.

^(a) Q_r is the rotational partition function. It does not take the hyperfine splitting into account and we took $J = 15.0$ as the maximum J value.

^(b) Q_v is the vibrational partition function. The total partition function of the molecule is $Q_r \times Q_v$. If the hyperfine structure is taken into account, QTOT should be multiplied by the nuclear spin statistics contribution.