REPORTING THE ROTATIONAL INVESTIGATION OF GLUTARONITRILE

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ABSTRACT

Formyl (HCO) molecules have been found in the interstellar medium (ISM) at least a dozen times so far, suggesting that there are more to be found. However, high-resolution spectroscopic data for these kinds of small molecular species are still lacking, making it difficult to detect them. Experiments were conducted to determine the rotational spectrum of glutaronitrile. An FTM spectrometer was used to study the rotational spectra of glutaronitrile's supersonic jet between 6 and 20 GHz. In addition, the mmW spectrum was detected in the frequency range 72−116.5 GHz using a broadband millimetre-wave spectrometer based on radio astronomy receivers with rapid Fourier transform backends. Calculations at the highest degree of ab initio were used to support the spectroscopic searches. The gg conformer of glutaronitrile was found to have 111 rotational transitions with maximal J and Ka quantum numbers of 54 and 18, respectively. We were able to precisely calculate the rotational, nuclear quadrupole coupling, quartic, and sextic centrifugal distortion constants thanks to the study we carried out on the data. In the search for glutaronitrile in the cold and warm molecular clouds Orion KL, Sgr B2(N) and TMC-1, these rotational parameters were used. These spectral scans were collected by IRAM 30 m at 3 mm. There was no Glutaronitrile identified, and the column densities of the upper limits were established. Sgr B2 and Orion KL total column densities are 1.5 and 5 lower, respectively, than those for the comparable succinonitrile in Orion KL.

Keywords: Glutaronitrile, Wavefunction, Spectrum, molecules, Rotational.

I. INTRODUCTION

In the ISM or circumstellar shells, scientists have found more than 200 different molecular species. Of them, 12 have been shown to have a similar structural unit, the formyl moiety, HCO. This set of compounds comprises seven aldehydes (-CHO), the simplest carboxylic acid, formic acid (HOCHO, two amides (-NCHO), formamide and N-methyl formamide, and two formates (-OCHO), methyl formate and ethyl formate. The interstellar aldehydes found so far include formaldehyde (HCHO), acetaldehyde (CH3CHO), cyanoformaldehyde (NCCHO), propynal (HC2CHO), propenal (H2CHCHO), propanal (CH3CH2CHO), and glycolaldehyde (HOCH2CHO) (HOCH2CHO). There are no known interstellar production paths for some aldehydes since existing theoretical chemistry models cannot adequately simulate their relative abundances. It is consequently not uncomplicated to draw predictions as to which yet-undiscovered species may be common in the interstellar medium (ISM) (ISM). Although several HCO-containing molecules have been found in space, it is reasonable to assume that there might be more.

Five of the seven aldehydes discovered in the ISM are alkyl derivatives of the simplest aldehyde,

formaldehyde. Hence, one possibility yet to be detected consists of an aldehyde carrying a cyclic functional group, either an aliphatic or aromatic ring. While the astrochemical literature on aromatic rings is rich, little material is available pertaining to aliphatic rings. Because it lacks a dipole moment, cyclopropane (c-C3H6) cannot be identified in rotational spectra as the smallest saturated carbon ring. Contrary to popular belief, cyclopropanecarboxyaldehyde (c-C3H5CHO, referred to as CPCA from now on) is an excellent choice for rotational spectrum observation.

Thanks to improvements in laboratory astro chemistry and the creation of radio telescopes with unprecedented sensitivity regimes, we're learning more and more about the chemistry of star-forming regions. The study of so-called complex organic compounds, which are carbon-based molecules with more than six atoms, is a major focus of modern astrochemical research (see McGuire 2018 for a census). Aldehydes are among the most common in nature, and they serve as precursors to a wide range of physiologically important compounds. Fifty years ago, the finding of formaldehyde (H2CO), the first interstellar aldehyde, in different galactic and extragalactic radio sources using the NRAO 140 ft telescope. Since then, several CHO-bearing species

with increasing levels of complexity have been discovered, mainly toward the giant molecular cloud complex Sagittarius B2 (Sgr B2), notably acetaldehyde, glycolaldehyde ($CH_2(OH)CHO$; Hollis et al. 2000), which is the simplest sugarrelated molecule, propanal (CH_3CH_2CHO; Hollis et al. 2004), and cyanoformaldehyde (CNCHO) (CNCHO). More complicated aldehydes such as lactaldehyde ($CH_3CH(OH)CH(O)$, which is the rational step up in complexity from glycolaldehyde, are yet to be found.

II. EXPERIMENTAL PROCEDURES

Firstly, the rotational spectrum of glutaronitrile was examined using a Balle-Flygare narrow-band-type FTMW spectrometer operating in the frequency area of 4–40 GHz. A commercial sample of glutaronitrile was utilized without any additional purification. A little amount of glutaronitrile sample was put in a liquid reservoir which was heated at roughly 75∘C to achieve appropriate vapour pressure. The reservoir was filled with Ar gas and pressurised to 0.8 bars before the pulsed valve was turned on. Fabry-Pérot resonator cavity was used to resolve minor hyperfine splittings by supersonically expanding a glutaronitrile-in-Ar mixture between two mirrors using a pulsed valve placed parallel to the resonator. After that, the glutaronitrile molecules are rapidly cooled to a rotational temperature of ∼2 K so that they may be studied via FTMW spectroscopy. The frequency measurements are expected to have an accuracy of more than 3 kHz and a resolution superior to 5 kHz. A spectrometer built at the Yebes Observatory (Spanish National Geographic Institute (IGN)) captured the rotating emission spectra of glutaronitrile at room temperature from 72 to 116.5 GHz in the second half of the experiment. The rotating spectrometer has radio receivers similar to those used in radio astronomy to look for chemical emission in outer space on board the broadband high resolution spectrometer. The W band (72–116.5 GHz) rotational transitions may be seen using 16×2.5 GHz fast Fourier transform spectrometers (FFTs) with a spectral resolution of 38.14 kHz. The spectrometer's cell is a 890 mm long by 490 mm wide stainless steel cylinder, with the long axis horizontally oriented. We used dry heating tape and a PID (proportional integral derivative) temperature controller to heat the glutaronitrile sample to 80°C in a PyrexTM vacuum Schlenk. The injection line was held at 80°C to prevent sample condensation during the experiment. For the continuous flow experiment, the vacuum chamber was set to a constant pressure of 7.0×10^3 mbar before the sample was introduced since higher pressures create unwanted line broadenings. With the given working pressure, the rotational lines of glutaronitrile have a HWHM of 0.3−0.45 MHz, which is well fitted to frequency measurements with high precision. The observation approach used in all of these tests was frequency switching with a throw of 25 MHz.

III. ROTATIONAL SPECTRUM AND ANALYSIS

The gg species of glutaronitrile, the global minimum and hence the most likely candidate for detection by its rotational spectrum, may take on four conformers in the gas phase. This conformer is a near prolate molecule that has a C2 symmetry axis, which corresponds with its molecular b axis, and hence it has just one dipole moment component. With Ka = 0, 1, we detected very near rotational transitions of the b-type R-branch. They were tasked with finding and improving upon existing transition frequency estimations. That way, we could measure transitions with Ka = 2 in the b-type R branch as well as Ka = 1 through 3 on the b-type Q branch. The 33,1 32,2 rotational transition being divided into many hyperfine components due to the nuclear quadrupole coupling effects induced by the presence of two equivalent nitrogens. The nuclear spin moments are coupled to the overall rotational momentum by their interactions with the electric field gradient formed by the other molecular charges at the nuclei of these quadrupole moments. In all us detected 228 hyperfine components corresponding to 24 pure rotational transitions (see TABLE 1). (See TABLE 1). With the SPFIT software, we calculated the rotational, centrifugal, and nuclear quadrupole coupling constants for asymmetric top molecules using a Watson's A-reduced 1A' Hamiltonian: Rotational and centrifugal distortion parameters are contained in HR, and quadrupole coupling interactions are contained in HQ. Quantum numbers J, Ka, Kc, I, and F identify the energy levels involved in each transition, with I = IN1 + IN2 and F = J + I, with I = 0, 1, and 2. As a result of the investigation, the experimental constants and theoretical data provided in TABLE 2 were obtained. Comparison of the empirically observed rotational constants with those predicted ab initio leads to the clear identification of conformer gg. It can be shown from TABLE 2 that the estimated ab initio geometry is reasonably precise, with standard deviations of less than 0.7 percent. In spite of the fact that significant disparities can be detected between the experimental and theoretical centrifugal distortion constants, the agreement can be deemed good as the estimate technique of these parameters is not straightforward.

Finally, it can be observed that the nuclear quadrupole coupling constants coincide quite well with those anticipated theoretically.

We began looking for rotational transitions of higher energy conformers, such as gt species, once the gg conformer had been designated. According to its relative energy, its estimated population (at the cell's temperature, 300 K) is ∼1/3 of that of gg conformer but taking into account the values of dipole moment components predicted by ab initio calculations, the expected intensity of its rotational transitions is ∼1/5 of those observed for gg conformer. We looked for gt conformer-related lines in the anticipated frequency ranges, but none were discovered. Given the strong signalto-noise ratio for the rotational transitions of the gg conformer discovered by FTMW spectroscopy, it seems that gt should be likewise identified. Collisional relaxation of the gt conformer to the gg form, via a low-energy inter conversion barrier, is one possible explanation for the lack of the gt conformer in the supersonic jet. Collisions between the various conformers and the buffer gas molecules take happen early in the supersonic expansion to bring about this process. When the isomerisation barrier is about 500–600 cm1 and Ar is utilised as the carrier gas, it has been demonstrated that collisional removal of a higher energy conformer is conceivable. To obtain some understanding, we estimated the potential energy profile between the gt and gg conformers by scanning the dihedral angle ∠ C1C2C3C4. An energy barrier of 698 cm−1 was identified, at the CCSD/cc-pVTZ level of theory, implying a collisional relaxation, at least partial, from gt to gg conformer. As a result, there is a lower than predicted gt conformer population, making it unable to observe rotational transitions.

Table 1: Rotational transitions for glutaronitrile observed by FTMW spectroscopy

J' [a]	K_a'	K_c'	I'	F'	J''	K_a''	K_c''	I''	F''	Freq. meas. [b] (MHz)	Uncert. [c] (MHz)	Obs.-calc. [d] (MHz)
2	2	0	2	4	2	1	1	2	4	9523.644	0.005	0.000
2	2	0	1	3	2	1	1	1	3	9523.754	0.005	−0.000
2	2	0	1	1	2	1	1	1	1	9523.848	0.005	0.001
2	2	0	2	3	2	1	1	2	3	9523.866	0.005	0.001
2	2	0	2	2	2	1	1	2	2	9523.943	0.005	0.001
2	2	1	0	2	2	1	2	0	2	9919.754	0.005	−0.000
2	2	1	1	2	2	1	2	1	2	9919.807	0.005	−0.003
2	2	1	2	4	2	1	2	2	4	9919.886	0.005	−0.003
2	2	1	1	3	2	1	2	1	3	9920.044	0.005	−0.000
2	2	1	1	1	2	1	2	1	1	9920.178	0.005	0.004
2	2	1	2	3	2	1	2	2	3	9920.199	0.005	−0.001
2	2	1	2	2	2	1	2	2	2	9920.309	0.005	0.001
2	1	2	2	1	1	0	1	2	1	9103.868	0.005	0.002
2	1	2	1	1	1	0	1	1	1	9103.879	0.005	0.002
2	1	2	0	2	1	0	1	2	1	9103.891	0.005	0.001
2	1	2	2	3	1	0	1	2	3	9103.926	0.005	−0.001
2	1	2	1	3	1	0	1	1	2	9104.052	0.005	−0.003

We estimated the transition frequencies of glutaronitrile's gg conformer in the mmW frequency range using rotational and centrifugal distortion constants found by FTMW measurements. An initial assignment was established simply by identifying the b-type R-branch transitions with Ka = 0,1. b-type R-branch rotational transitions up to Ka = 3 and Q-branch rotational transitions up to Ka = 17,18 were also included in the study. A total of 89 rotational transitions, see Table 3, were recorded in the mmW range and fitted to a Watson's A-reduced 1A' Hamiltonian. Table 2 summarizes the results of the investigation. In addition to the rotational and quartic centrifugal distortion constants previously found by FTMW experiments, the sextic centrifugal distortion constants ΦK, ΦKJ , and φJK were determined. The inclusion of these factors in the fit marginally impacts the value of the rest of the floated parameters, as can be observed if data for the FTMW and mmw fits are compared.

TABLE 2: Molecular constants for glutaronitrile

Constants/units	FTMW fit	Global fit	mmW fit	Theory [a]
A/MHz	4756.13738(24)	4756.1397(30)	4755.60(11)	4767.1
B/MHz	1582.79295(64)	1582.7606(25)	1582.7530(84)	1571.6
C/MHz	1449.29522(55)	1449.27921(65)	1449.28150(85)	1439.5
Δ_J/kHz	2.4036(64)	2.3447(16)	2.3555(52)	2.2839
Δ_K/kHz	56.221(24)	59.787(41)	57.89(39)	35.8181
Δ_{JK}/kHz	−19.905(21)	−20.4772(93)	−20.486(11)	−21.7187
δ_J/kHz	0.5920(32)	0.54303(77)	0.5477(25)	0.3213
δ_K/kHz	4.54(26)	4.282(45)	4.78(14)	5.3779
Φ_K/Hz	–	6.680(87)	4.40(47)	1.3457
Φ_{KJ}/Hz	–	−1.834(17)	−1.804(21)	−1.2627
ϕ_{JK}/Hz	–	−0.112(17)	−0.110(30)	−0.5042
χ_{aa}/MHz	−0.4123(10)	–	–	−0.4126
χ_{bb}/MHz	0.0989(15)	–	–	0.1045
σ_{rms}/kHz	3.44	38.10	42.33	–
σ_{wrms}	0.60 [b]	0.76 [c]	0.84 [c]	–
N_{lines}	228 [d]	111	89	–
J_{min}/J_{max}	0/5	0/54	24/54	–
$K_{a,min}/K_{a,max}$	0/3	0/18	0/18	–

Table 3: Rotational transitions for glutaronitrile observed in the mmW region

J' [a]	K_a'	K_c'	J''	K_a''	K_c''	Freq. meas. [b] (MHz)	Uncert. [c] (MHz)	Obs.-calc. [d] (MHz)
40	1	40	39	0	39	116272.079	0.050	−0.010
40	0	40	39	1	39	116271.949	0.050	0.016
39	2	38	38	1	37	114711.079	0.050	−0.038
39	1	38	38	2	37	114700.167	0.050	−0.033
39	1	39	38	0	38	113397.853	0.050	0.018
39	0	39	38	1	38	113397.669	0.050	0.041
38	2	37	37	1	36	111839.559	0.050	−0.023
38	1	37	37	2	36	111824.587	0.050	−0.021
38	1	38	37	0	37	110522.432	0.050	0.023
38	0	38	37	1	37	110522.139	0.050	0.023
36	1	36	35	0	35	104768.151	0.050	−0.009
36	0	36	35	1	35	104767.553	0.050	−0.020

Collisional relaxation between conformers is not conceivable in the GACELA experiments since they are not done in a supersonic expansion environment. Hence, the rotational transitions for gt conformer should be seen in our mmW spectra with intensity five times less than those for the gg conformer. However, the signal-to-noise ratio of the gg conformer is considerably smaller in the mmW area than that discovered in the FTMW studies, and then, the rotational lines for gt conformer could not be differentiated from the noise level.

Because glutaronitrile possesses two identical N nuclei with an I = 1 spin, the FTMW spectrometer was able to detect nuclear quadrupole coupling hyperfine splittings. However, in the mmW range, all the measured lines were viewed as single lines, and no hyperfine splitting could be identified since they are smaller than the experimental widening of the lines. The rotational spectrum in the mmW area,

nevertheless, indicates the effect of nuclear spin statistics on the transition intensities. This is related to the shape of the molecule, which permits an interchange of identical particles by the rotation around one of the primary axes. C2's C2b operation, which is equal to rotating the b-axis by radians, involves exchanging the locations of three non-equivalent hydrogen pairs (fermions with I = 1/2) and two nitrogen atoms (bosons with I = 1) in the molecule at the same time. Fermi-Dirac statistics must be evaluated due to the presence of three pairs of fermions and the bosons. Hence, the whole wavefunction, given as ψtot = ψeleψvibψrotψns, must be antisymmetric with regard to the C2b operation. The related wavefunctions ψele and ψvib for the ground electronic and vibrational states are symmetric. For levels where $K_a + K_c$ = even, the rotational wavefunction rot has an antisymmetric parity, but for levels where $K_a + K_c$ = odd, it has a symmetric parity. Nuclear spin functions must be

paired with rotational wavefunctions of opposite symmetry in order to fulfil Fermi-Dirac statistics. The overall nuclear statistics weights are $(2I_H + 1)2 (2I_H + 1)^2 (2I_H + 1)^2 (2I_N + 1)^2 = 576$, and the nuclear statistical weight for the rotational levels with $K_a + K_c$ = even and odd is 23 and 25, respectively.

Table 4: Rotational partition functions for glutaronitrile at different temperatures.

Temperature/K	Q_r
300.000	223332.4
225.000	158807.8
150.000	92210.4
75.000	33259.6
37.500	11747.9
18.750	4152.4
9.375	1469.2

A composite fit employing all the transition frequencies from both FTMW and mmW observations were done. As well as the other fits and theoretical computations, the gg conformer's spectroscopic constants are provided in TABLE 2. Because of this, we were able to replicate higher frequency glutaronitrile spectra by using the constants produced from the combined fit in the MADEX algorithm. The frequency predictions for glutaronitrile up to 300 GHz determined at T = 300 K. To estimate the column density of glutaronitrile, we utilized the partition function values provided in Table 4, which were obtained incorporating rotational levels at maximum value of J = 90.

IV. CONCLUSIONS

The current study covers the investigation of the rotational spectra of a novel dinitrile, glutaronitrile. The microwave and millimeter-wave spectra were measured using two distinct spectroscopic techniques: an FTMW spectrometer at low frequencies and a broadband millimeter-wave spectrometer in the frequency range 72–116.5 GHz. From the analysis of the spectra, we obtain accurate rotational parameters for the most stable conformation, named the gg species, which were used to unsuccessfully search for glutaronitrile in the cold and warm molecular clouds Orion KL, Sgr B2(N), B1-b, and TMC-1, using the spectral surveys captured by IRAM 30 m at 3 mm.

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