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Philipp Buschmann, Kevin G Lengsfeld, Kathryn Aydt, Michaela K Jahn, Sven Herbers, et al.. Proton inversion tunneling in the rotational spectrum of acetone cyanohydrin. Journal of Molecular Spectroscopy, 2020, 373, pp.111372. 10.1016/j.jms.2020.111372 . hal-03182486

Graphical Abstract

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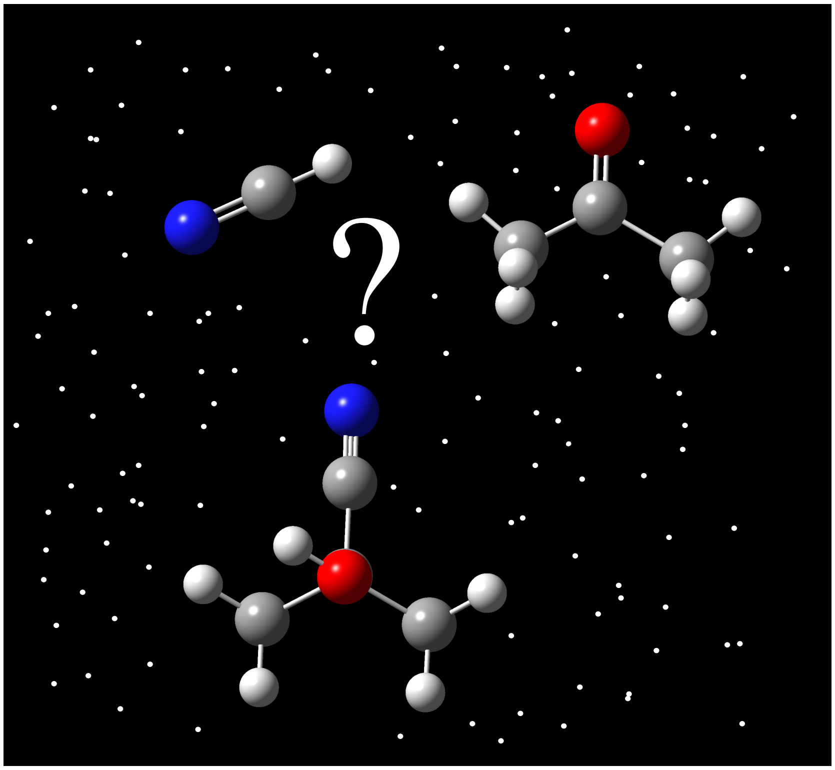

Highlights

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- first reported high resolution microwave spectrum of acetone cyanohydrin
- first characterization regarding Coriolis and hyperfine structure
- revealing complexity due to large amplitude motions

Proton Inversion Tunneling in the Rotational Spectrum of Acetone Cyanohydrin

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Abstract

Rotational transitions of the *gauche*-acetone cyanohydrin are measured in the microwave range between 5 and 23 GHz. Results from quantum chemistry indicate that the hydrogen atom of the hydroxyl group undergoes a tunneling motion connecting two equivalent structures. The observed signals are assigned to the two lowest tunneling substates 0^+ and 0^-, belonging to either *a*- or *c*-type transitions exhibiting Coriolis splittings of a few MHz. Additional hyperfine structure arises from quadrupole coupling of the ^{14}N nucleus. The energy separation ΔE of the 0^+ and 0^- states is calculated to be around 51 GHz. The molecular structure and internal dynamics are discussed in terms of their spectral signatures.

Keywords:
Coriolis coupling, astrochemistry, high resolution microwave spectroscopy, prebiotics, cyanohydrin

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1. Introduction

Where do we come from? This is a genuine question. Until today, we are still questioning whether the first prebiotic molecules on Earth were formed

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in its atmosphere, or if they were brought to Earth by asteroids billions of years ago. Humanity has always been fascinated by the firmament, leading to intense research in the fields of astrochemistry, astrobiology, and astrophysics.

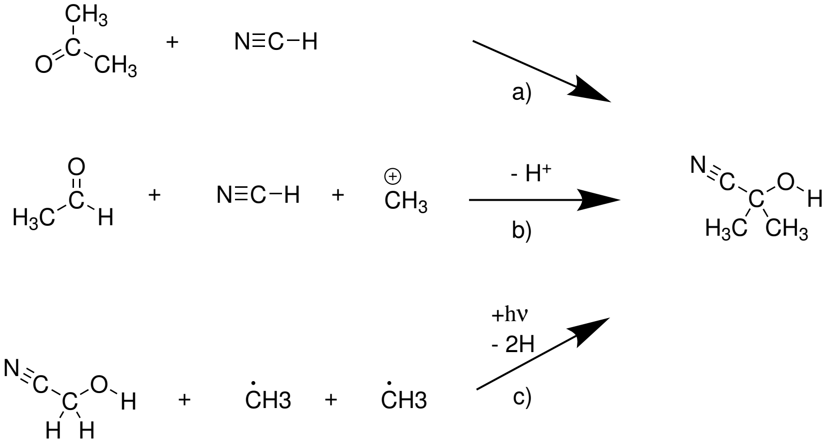
Finding or dismissing evidence for the astrochemical models and their understanding is a key aspect of radioastronomic observations in combination with theoretical knowledge and measurements under well defined conditions in terrestrial laboratories. Since most of the molecules in space are unambigously identified by their rotational transitions, microwave and millimeter wave spectroscopy are the established methods of choice. Concerning chiral discrimination of different enantiomers, although sophisticated concepts for laboratory experiments are developed, seems illusive.[1] Only one chiral molecule, propylene oxide (CH_3CHCH_2O), has been detected in molecular clouds yet, while it is also unknown, if these molecules are formed enantioselective or racematic.[2] On Earth, it is well known that most reactions do not produce only one enantiomer as a product without adding chiral information e.g. a well defined catalyst. Even when acknowledging parity violation caused by the weak interaction, it is likely too inefficient to see these reactions take place in molecular clouds on their own. Such reactions might occur on a catalytic surface, that is presumably dust in molecular clouds, that might aggregate over long time scales forming comets and asteroids in the end. This allows for two possibilities: Outgasing of comets can be detected and these signals can be analyzed and assigned. A well known example is the comet Hale-Bopp, that has been studied extensively.[3, 4, 5, 6] This approach is quite limited, since the object has to be near to the earth (e.g. in our solar system), to allow for in-situ observations. Another approach is the observation of molecular clouds and try to find molecules, that have potential to form chiral prebiotic molecules like amino acids, sugars etc.[7] Therefore, it seems more promising to look for small molecules as potential precursors for prebiotics or chiral molecules themselves. This is also the purpose of our investigation.

With more than 200 different molecular species positively detected, nearly fifty percent of these molecules can be classified as diatomics and triatomics, that in certain cases are common and important for the production of medium sized molecules.[8] The laboratory formation of the already detected molecules might be quite different from their formation in space: Small metal containing molecules are often vaporized into the gas phase by laser ablation. Radical and ion formations require electric discharge, which can also be applied to form long conjugated unsaturated carbon chains like cyanopolyynes which were identified very early in molecular clouds [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32]. Nevertheless, many detected molecules are stable under laboratory conditions, for example aldehydes[33, 34, 35, 36, 37, 38, 39, 40, 41], ketones [42, 43, 44], esters [37, 45, 41], amides [46, 47, 39, 36], carboxylic acids [48, 49], amines [50, 51, 52], alcohols [53, 54, 55, 56, 57, 58] and nitriles [51, 59, 34, 60, 61, 62, 41, 63] .

Acetone has been identified already in 1987 in Sgr B2 as an astrochemically abundant molecule, which was confirmed in 2002 [64]. Later, Friedel et al. and Lykke et al. found acetone signals in Orion KL and around the low mass protostar IRAS 16293-2422 [65, 66]. The other prerequisite component, hydrogen cyanide, is quite common in most regions of the interstellar medium [67]. In the laboratory, direct reaction of acetone with hydrogen cyanide results in the creation of the metastable molecule, acetone cyanohydrin, which is discussed to be a prochiral precursor. Since the labotatory reaction (reaction (a) in Scheme 1) will largely be inhibited in space due to its high Gibbs free activation energy, we suggest different possible reaction pathways : The formation of acetone cyanohydrin from the reaction of hydrogen cyanide and acetaldehyde (reaction (b) in scheme 1) with highly reactive methyl radicals or cations. The methylation process is assumed to be the initial step for the interstellar formation of protonized acetone and subsequent addition of hydrogen cyanide in the same environment result in the formation of acetone cyanohydrin after proton abstraction [68]. The stepwise methylation of formaldehyde cyanohydrin/hydroxyacetonitrile (reaction (c) in scheme 1) upon subsequent exchange of two hydrogens by two methyl groups via radical mechanisms could also form acetone cyanohydrin. Alternatively, such two step substitutions could also be applied to two other possible starting materials ethanol and ethyl cyanide.

The simplest cyanohydrin, Hydroxyacetonitrile, was discovered in 2019 around the protostar IRAS16293-2422 B [69], two years after its laboratory characterization in the millimeter wave region based on microwave data from Cazzoli et al. and Lister et al.[70, 71, 72] This molecule is proposed to be a key in the synthesis of prebiotic significant molecules.[73]

With 13 atoms, like benzonitrile [74, 75], acetone cyanohydrin, would be one of the largest molecular species found in the interstellar medium, apart from the purely carbon based buckyballs C_{60} and C_{70}. In addition to the fullerenes, which due to the lack of a dipole moment could only be identified like the benzene molecule by their vibrational bands [76, 77, 78], efforts have been made to find polyclic aromatic hydrocarbons. The targeted



Scheme 1: Possible reactions to form acetone cyanohydrin.

species were chosen to that have comparably large dipole moments, like the notable example of corannulene, but those attempts have not been successful yet.[79, 80]

2. Methodology

2.1. Theoretical

Acetone cyanohydrin was studied in 1977 by Lister and Lowe using Stark modulated microwave spectroscopy [81]. The authors only observed one series of *a*-type *R*-branch bands which allowed them to determine just the three rotational constants of the vibrational ground state ($A_0 = 4748.4$ MHz, $B_0 = 2830.83$ MHz, $C_0 = 2762.99$ MHz). By comparing the corresponding moments of inertia with those predicted using a molecular model based on the structures of *tert*-butyl cyanide and methanol, Lister and Lowe concluded that the assigned signals belong to the *gauche* conformer with the structure given in Figure 1.

To investigate the conformations of acetone cyanohydrin, we perform a potential scan rotating the hydroxyl group around the C-O bond using the B3LYP functional, an aug-cc-pVTZ basis set, Grimmes D3 corrections, and Becke-Johnson damping as implemented in the Gaussian 16 program revision B.01 [82], as illustrated in Figure 2. The potential energy curve reveals two stable conformers where the hydrogen atom of the hydroxyl group is in

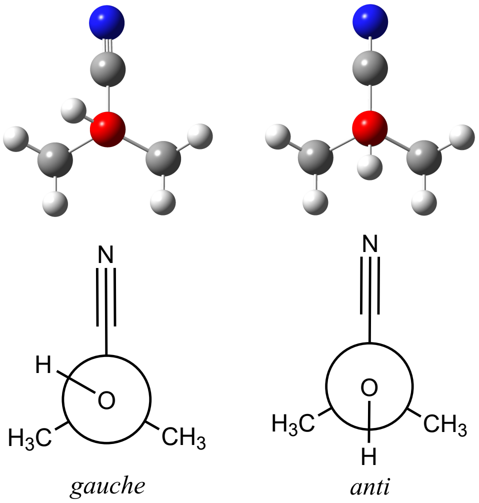


Figure 1: Molecular structures of two conformers of acetone cyanohydrin and their corresponding Newman projections.

gauche or in *anti* position with respect to the cyano group. Geometry optimizations at the B3LYP-D3BJ/aug-cc-pVTZ level of theory are carried out to obtain fully relaxed structures of the two conformers, as well as anharmonic frequency calculations for the ground state rotational constants and centrifugal distortion constants.

Chemical intuition might suggest the *anti*-conformer to be favored in view of the interactions between the lone pairs of the oxygen and the methyl groups. However, in acetone cyanohydrin as well as other alcohols with two identical substituents bonded to the hydroxyl carbon making the two *gauche* structures are energetically equivalent, are ethanol, propanol, propargyl alcohol, benzyl alcohol, methoxymethanol, allyl alcohol and some of their derivatives [83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95], the anti-confomer is higher in energy. Figure 2 illustrates the barrier hindering the tunneling large amplitude motion (LAM) between the two equivalent *gauche* forms. Consequently, due to the transition dipole selection rules, all *b*-type transitions of *gauche* acetone cyanohydrin appear as tunneling doublets corresponding to inter-state transitions with separation of $2\Delta E$, while the *a*- and *c*-type intrastate transitions only show narrow splittings caused by Coriolis interactions.

2.2. Experimental

All measurements were performed using a Fourier transform microwave spectrometer with a coaxially oriented beam resonator arrangement (COBRA), characterized by its high sensitivity and resolution, that allows to distinguish two signals separated by $> 5\,\text{kHz}$ [96]. Acetone cyanohydrin was measured maintaining continuous cooling to slow down decomposition of the substance into acetone and hydrogen cyanide. Adiabatic supersonic jet expansions with neon or helium as carrier gases were obtained from the nozzle of a pulse solenoid valve operated at a stagnation pressure of approximately 1 bar.

3. Results and Discussion

3.1. Prediction

The computed molecular rotational-torsion parameters are collected in Table 1. The barrier heights hindering the internal rotations of the two methyl groups were predicted to be $1262\,\text{cm}^{-1}$ and $1143\,\text{cm}^{-1}$ for the *gauche* conformer. For the two equivalent methyl rotors of the *anti* conformer, the calculation obtained a value of $1255\,\text{cm}^{-1}$. These values correspond with a very small tunneling rate. Indeed predictions with the combined axis method Hamiltonian in the *XIAM* program [97] confirm that the splittings resulting from the internal rotation for both conformers are below the resolution limit of the instrument.

The relaxed potential energy surface scan around the C-O bond, displayed in Figure 2, shows that the *gauche* conformer is about $670\,\text{cm}^{-1}$ more stable than the *anti*-conformer. Therefore, the strongest signals in the spectrum are expected to belong to *gauche* acetone cyanohydrin, even though the tunneling LAM, the nuclear quadrupole coupling, and the dipole moment being lower than that of *anti* acetone cyanohydrin, result in a reduction of the transition intensities.

For a convenient treatment of the hydroxyl LAM, we estimated the ΔE parameter by assuming a general exponential correlation between ΔE and the corresponding barrier height V of the equivalent *gauche* forms with data from literature. Therefore we perform a linear regression with these data, shown in Figure 3:

$$\ln(\Delta E/\text{GHz}) = -0.007298301 \times (V/\text{cm}^{-1}) + 7.171727$$

Table 1: Predicted molecular parameters of the two conformers of acetone cyanhydrin obtained at the B3LYP-D3BJ/aug-cc-pVTZ level of theory.

		gauche	*anti*
A_0 [a]	/ MHz	4726.67	4716.59
B_0 [a]	/ MHz	2828.84	2830.42
C_0 [a]	/ MHz	2760.76	2775.90
D_J [b]	/ kHz	0.3182	0.3156
D_{JK} [b]	/ kHz	4.3024	4.0432
D_K [b]	/ kHz	-3.5157	-3.2378
d_1 [b]	/ Hz	-6.9102	-5.0884
d_2 [b]	/ Hz	-1.644	-1.106
$3/2\chi_{aa}$ [c]	/ MHz	-7.205	-7.220
$1/4(\chi_{bb} - \chi_{cc})$ [c]	/ MHz	-0.1008	-0.1233
χ_{ab} [c]	/ MHz	-0.0222	-
χ_{ac} [c]	/ MHz	0.0131	-0.167
χ_{bc} [c]	/ MHz	0.0349	-
$V_{3,\alpha}(\mathrm{CH_3})$ [d]	/ cm^{-1}	1262	1255
$s_\alpha(\mathrm{CH_3})$[e]		103.3	102.7
$V_{3,\beta}(\mathrm{CH_3})$ [d]	/ cm^{-1}	1143	1255
$s_\beta(\mathrm{CH_3})$[e]		93.6	102.7
$\lvert\mu_a\rvert$ [f]	/ D	3.1	4.8
$\lvert\mu_b\rvert$ [f]	/ D	1.2	0.00
$\lvert\mu_c\rvert$ [f]	/ D	0.7	1.5
E [g]	/ kJ/mol^{-1}	0	7.55

[a] Rotational constants in the vibrational ground state.

[b] Quartic centrifugal distortion constants, in Watson S reduction, I^r representation.

[c] Quadrupole coupling tensor elements in the inertial principal axis system.

[d] V_3 potential of the methyl torsion predicted by relaxed scans. The indices α and β refer to the two methyl groups.

[e] Reduced barriers: $s := \frac{4}{9}V_3/F$; F is the rotational constant of the methyl rotor

[f] Dipole moment components in the inertial principal axis system

[g] Energy relative to the absolute energy (zero-point corrected) of -286.728491758 E_h of the more stable *gauche* conformer.

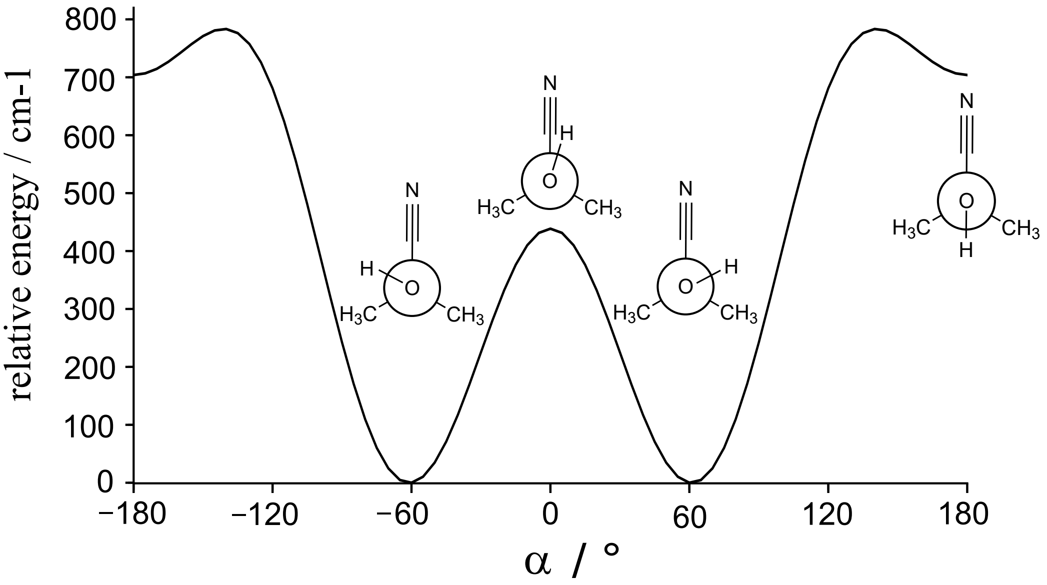


Figure 2: Potential energy curve for the rotation of the hydroxyl group of acetone cyanohydrin calculated at the the B3LYP-D3BJ/aug-cc-pVTZ level of theory. Important conformers are displayed by Newman projections.

The computed value for the barrier height of aceton cyanohydrin (approximately 444 cm^{-1}) then corresponds to a ΔE value of 50.972 GHz.

3.2. Fits

Initially, measured a-type transitions of *gauche* acetone cyanohydrin revealed, in addition to the quadrupole hyperfine structure, splittings due to Coriolis interactions. The two components corresponding to the intra-state transitions of the hydroxyl torsional states 0^+ and 0^- were unambiguously assigned based on their similar hyperfine structures and fitted together utilizing a suitable Hamiltonian implemented in the CALPGM suite of programs by Pickett [102]. After the spectroscopic parameters have been adjusted, also weaker c-type transitions were included in the analysis. All of the strongest signals observed in the frequency range of our spectrometer were assigned, lacking any sign of b-type transitions. Fitting the rotational constants and the ^{14}N nuclear quadrupole coupling parameters $3/2\chi_{aa}$ and $1/4(\chi_{bb} - \chi_{cc})$ as well as Coriolis coupling constants and the energy separation ΔE leads to a root-mean-square (rms) deviation of 1.4 kHz close to the experimental accuracy of about 2 kHz. Fixing the ΔE parameter obtained by the linear

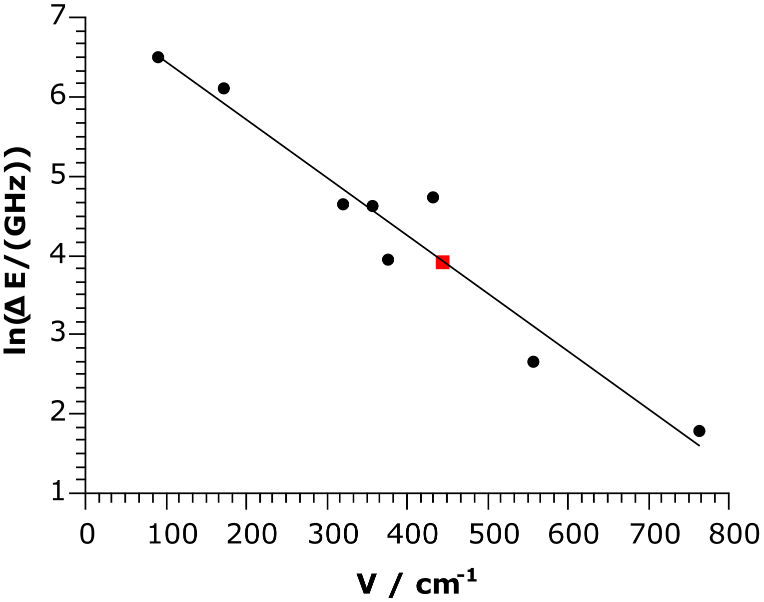


Figure 3: Plot of experimentally determined values of $\ln(\Delta E)$ against tunneling barrier heights of the alcohols listed in Table 2. The red square on the linear regression locates the ΔE value for the computed barrier height of the investigated acetone cyanohydrin.

Table 2: Experimentally deduced ΔE parameter and the corresponding barrier height of the hydroxyl group tunneling motion between the two equivalent *gauche*-forms of selected alcohols.

Molecule	V / cm^{-1}	ΔE / GHz
Propargyl alcohol [98]	90	644
Methyl hydroperoxide [99]	173	449
equatorial-1-Methylcyclohexanol [83]	320	103
axial-1-Methylcyclohexanol [83]	356	103
equatorial-Cyclohexanol [88]	377	52
syn-Allyl alcohol [84]	558	14
gauche-2,2,2-Trifluoromethanol [95]	763	6
Formaldehyde cyanohydrin [100]	433[a]	113
Acetone cyanohydrin	444[b]	51[c]

[a] from flexible model calculation [101]

[b] from ab initio calculation

[c] from linear regression, see Figure 3

regression results in the same rms value. To perform these fits, we used the effective Hamiltonian:

$$H = \sum_{\nu=0}^{1} |\nu\rangle(H_\mathrm{r} + H_\Delta + H_\mathrm{NQ})\langle\nu| + (|0\rangle\langle 1| + |1\rangle\langle 0|)H_\mathrm{c}$$

$\langle 0|$ and $\langle 1|$ denote the symmetric and the antisymmetric tunneling state, respectively. $\mathrm{H_r}$ consists of the overall rotation and the quartic centrifugal distortion terms and has the form:

$$H_\mathrm{r} = AP_a^2+BP_b^2+CP_c^2-D_JP^4-D_{JK}P^2P_z^2-D_KP_z^4+d_1P^2(P_+^2+P_-^2)+d_2(\hat{P}_+^4+\hat{P}_-^4),$$

where the terms A, B and C are the rotational constants of the vibrational ground state, D_J, D_{JK}, D_K, d_1 and d_2 describes the quartic centrifugal distortion coefficients of Watson's S-reduced Hamiltonian in the I^r representation (P_+, P_- are the step operators). The term H_{NQ} describes the quadrupole coupling

$$H_{NQ} = \frac{1}{2I(2I-1)} \sum_{\alpha,\beta} \chi_{\alpha\beta}[I_\alpha, I_\beta]_+ \quad \text{with} \quad \chi_{\alpha\beta} = e\mathbf{Q}q_{\alpha\beta} \tag{1}$$

where $\chi_{\alpha\beta}$ are the tensor elements proportional to the elementary charge e, the nuclear quadrupole moment $\mathbf{Q}$, and the electric field gradient tensor elements. I denotes the nuclear spin of the quadrupolar nucleus that couples with the end-over-end rotation J of the molecule.[103] This results in the total angular momentum quantum number $F = J + I$. In the coupled basis, the Hamiltonian is no longer diagonal in J, but diagonal in F, the latter only remaining a good quantum number if a significant amount second order contribution to the quadrupolar coupling occurs.

H_Δ describes the torsional splitting between the $\langle 0|$ and $\langle 1|$ tunneling state

$$H_\Delta = \Delta E + \Delta E_J P^2 + \Delta E_K P_z^2 + \Delta E_2 (P_+^2 + P_-^2),$$

and H_c is the Coriolis operator connecting the two states given by

$$H_c = F_{ac}(P_a P_c + P_c P_a) + F_{bc}(P_b P_c + P_c P_b).$$

The constants F_{ac}, F_{bc} are Coriolis coupling parameters, and E_J, E_K and E_2 are centrifugal distortion parameters to ΔE. [104, 105, 106] The spectroscopic parameters from the least squares fitting are presented in Table 3. All observed frequencies are available in Table S1 and Table S2 of the Supplementary Material.

The successful observation of the huge $2\Delta E$ tunneling splitting of the b-type signals in the spectrum would capture this value directly. Because of the splitting being larger than the total span of the centimeterwave region, measurements in the millimeterwave region would be required to determine ΔE from a splitting. All transitions observed in the microwave spectrum belong to the *gauche* conformer, indicating that *anti* acetone cyanhydrin is too high in energy and not present under our measurement conditions.

3.3. Internal rotations

In agreement with results for the barrier height from quantum chemistry, splittings arising from the internal rotations of two methyl groups could not be resolved. Barriers close or above $1000\,\mathrm{cm}^{-1}$ are typical for methyl groups at the end of an alkyl chain with ethane as the simplest example [107], commonly resulting in the symmetry species being split at or below the resolution limit.[108, 109, 110, 111, 112] The V_3 potential barriers of methyl groups in three series of increasingly methyl substituted alcohols are collected in Table

Table 3: Molecular parameters of the *gauche* acetone cyanohydrin from the rotational transitions fitted with a suitable Hamiltonian utilizing the program SPFIT.

Parameter	Unit	Fit 1	Fit 2
A_0 [a]	/ MHz	4777.45751(52)	4777.45753(52)
B_0 [a]	/ MHz	2830.83663(15)	2830.83666(15)
C_0 [a]	/ MHz	2762.93703(14)	2762.93702(14)
D_J [b]	/ kHz	0.2881(22)	0.2888(22)
D_{JK} [b]	/ kHz	4.5240(62)	4.590(21)
D_K [b]	/ kHz	-3.73(10)	-3.84(11)
d_1 [b]	/ kHz	-0.0103(27)	-0.0102(27)
d_2 [b]	/ kHz	-0.0152(13)	-0.0158(13)
$\frac{3}{2}\chi_{aa}$ [c]	/ MHz	-6.47730(77)	-6.47731(77)
$\frac{1}{4}(\chi_{bb}-\chi_{cc})$[c]	/ MHz	-0.07917(30)	-0.07918(30)
χ_{ab} [c]	/ MHz	-0.0222[j]	-0.0222[j]
χ_{ac} [c]	/ MHz	0.0131[j]	0.0131[j]
χ_{bc} [c]	/ MHz	0.0349[j]	0.0349[j]
ΔE [d]	/ MHz	50972[j]	49868(33)
F_{bc} [e]	/ MHz	3.461(24)	3.426(26)
F_{ac} [e]	/ MHz	-24.3494(29)	-24.048(90)
E_J [f]	/ MHz	0.027726(42)	0.027661(47)
E_K [f]	/ MHz	-0.04634(11)	-0.04635(11)
E_2 [f]	/ MHz	-0.034135(24)	-0.034161(26)
N [g]	/ MHz	170	170
σ [h]	/ kHz	1.40	1.35

[a] vibrational ground state rotational constants

[b] quartic centrifugal distortion constants Watson S reduction, I^r representation

[c] quadrupole coupling tensor elements in the principal inertial axis system

[d] energy separation between the 0^+ and 0^- level

[e] Coriolis coupling parameters

[f] Centrifugal distortion parameters to ΔE

[g] number of assigned hyperfine components

[h] standard deviation

[j] value fixed during the fit

Table 4: Experimentally determined barrier heights to methyl group internal rotation of selected molecules and computed value of acetone cyanohydrin.

Molecule	V_3 / cm^{-1}
Ethane [107]	1012(1)
Ethyl fluoride [113]	1171(7)
Ethyl chloride [114]	1260(3)
Ethyl bromide [115]	1282(41)/1276(40)
Ethyl iodide [116]	1267(52)
Ethyl isocyanide [117]	1167(18)
anti-Ethanol [53]	1173.76(220)
gauche-Ethanol [91]	1331
gauche-Isopropanol [118]	588
tert-Butanol [119]	443
Acetaldehyde cyanohydrin [100]	1310(30)/1510(30)
gauche-Acetone cyanohydrin	1262/1143
anti-Acetone cyanohydrin	1252

4. Within each group the medium to high barriers decrease substantially with increasing degree of methyl substitution. This can be rationalized by the decreasing relative hyperconjugation effect of the rotating methyl group, with increasing number of methyl substituents. The value found for acetaldehyde cyanohydrin compared to the values we determined for acetone cyanohydrin indicate that this electronic effect is less pronounced in the exceptionally high methyl torsional barriers of cyanohydrins.

3.4. Proton tunneling

Though we are not able to conclusively determine the tunneling barrier between the two equivalent forms of *gauche* acetone cyanohydrin due to the lack of observed *b*-type transitions, we can compare the quantum chemically computed barrier with barriers of related molecules in the literature (see Table 2).

The computed tunneling barrier of acetone cyanohydrin is somewhat smaller but not significantly different in magnitude from the interconversion between the two non-equivalent *gauche* conformers of about 400 cm^{-1} in acetaldehyde cyanohydrin and to the tunneling barrier of formaldehyde cyanohydrin, which we could derive from experimental data with Meyer's flexible model approach.[101] This indicates that substituting the methyl groups by hydrogen atoms and vice versa does not dramatically change the electronic environment of the cyanohydrin moiety, which is mainly governed by the electron withdrawing property of the nitrile group. This assumption is supported by comparison with ethane derivatives, where the α-carbon atom is substituted by an electron withdrawing group e.g. CN and OH, leading to a remarkable increase of the methyl torsional barrier in cyanohydrins (see Table 4). Furthermore, comparing the tunneling barriers in Table 2 provides insight into steric repulsion interactions in the vicinity to the hydroxyl group. Propargyl alcohol for example experiences a quite free internal rotation as no steric interaction between the hydroxyl group and the remaining molecule seems to be present. So this missing repulsive contribution appears to be crucial since the barrier of propargyl alcohol is already extremely low for alcohols in general. This comparison of barrier heights in Table 2 shows that the steric repulsion interaction in the case of acetone cyanohydrin seems to be the predominant contribution to the tunneling barrier, which is comparable to cyclohexanol with essentially the same barrier height.

3.5. ^{14}N nuclear quadrupole coupling

The coupling of an atomic nucleus with electric quadrupole moment depends on the electric field gradient at the nucleus and therefore can serve as a direct probe regarding the electronic environment of the atom, in this case the ^{14}N nucleus. This can be discussed in terms of hybridization and polarizations of the chemical bonds in which the atom is participating in. Townes and Dailey provided a model to analyze and interpret the quadrupole coupling tensor in terms of qualitative bonding concepts. The initial model was restricted to linear and symmetric rotors [120], and subsequently expanded to asymmetric rotors possessing two independent elements of the (diagonalized) coupling tensor [121, 122]. In this conventional Townes-Dailey approach, the tensor element χ_{zz} along the bonding axis is linked only to the ionic character of the bond, and the difference of the two remaining tensor elements $\chi_{xx} - \chi_{yy}$ are used exclusively to determine the π character of the bond. Novick proposed an extended version of the model, using information of the whole tensor to determine the bonding characters [123]. So far, the ^{14}N nuclear quadrupole coupling of nitrile groups were mainly interpreted for planar molecules like tricyanobenzenes and substituted cyanobenzenes. In those molecules, the CN bond is always expected to be polarized due to the difference in electronegativity of the two elements [124, 125], while the mesomeric character changes by interactions with the aromatic system to

Table 5: Experimentally determined quadrupole coupling tensor element χ_{zz} of selected cyanides, denoting the component of the diagonalized tensor along the C-N bond axis.

Molecule	χ_{zz} / MHz
HCN [126]	-4.7
Acetonitrile [127]	-4.5
Isopropyl cyanide [128]	- 3.9
tert-butyl cyanide [129]	-4.2
Ethyl cyanide [130]	-4.5
Acetone cyanohydrin	-4.3
Acetaldehyde cyanohydrin [100]	-4.6

which they are bound. For acetone cyanhydrin, we assume that the electronic withdrawal is mainly reflected in ionic rather than mesomeric changes of the CN bond. The only molecule where the extended model was applied for *sp*-hybridization, is the symmetric top acetonitrile [123]. The tensor elements χ_{zz} of the quadrupole coupling tensor aligned CN bond are collected for a few cyanide containing molecules in Table 4. Similar to the conventional Townes-Dailey approach, the χ_{zz} value is correlated to the ionic character of the bond. A decrease of χ_{zz} leads to an increasing negative charge of the nitrogen atom. Attributed to the σ character of the CN bond, that which is reflected in the χ_{zz} value, the nitrogen atom draws electron density away from the central carbon. This inductive effect of the cyanide group does not change dramatically upon substitutions of the carbon atom.

The conclusions are supported by Natural Bond Orbital (NBO) calculations shown in Figure 3. The effective electron transfers are quantified as $0.074\,\mathrm{e}$ and $0.054\,\mathrm{e}$ from the methyl group hydrogen atoms to the central carbon and $0.272\,\mathrm{e}$ and $0.073\,\mathrm{e}$ from central carbon to the hydroxyl and the cyano group, respectively. Taking the partial charges of the cyano group yields $0.359\,\mathrm{e} - 0.286\,\mathrm{e} = 0.073\,\mathrm{e}$. This indicates that electron withdrawing effects of the hydroxyl group is mainly responsible for the positive charge at the central carbon atom. On the other hand, the predominant contribution to the high methyl torsional barrier is the repulsive interactions between the methyl hydrogen atoms and the remaining substituents, as shown in the methyl torsion potential given in Figure 5. A similar situation was observed in the case of methyl 3,3,3-trifluoropyruvate, where repulsive interactions of the methyl group with the carbonyl oxygen of methylesters explain the changes in barrier heights with different substitutions [131].

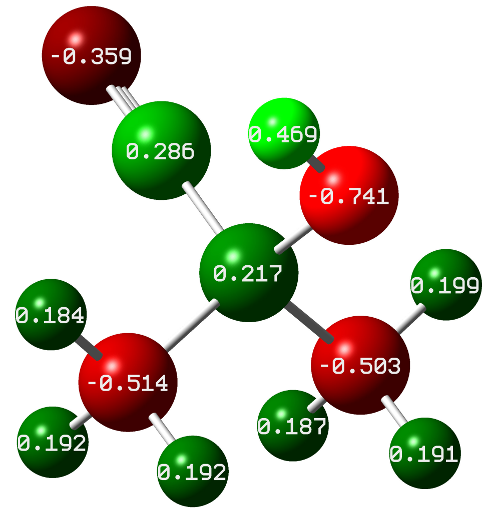


Figure 4: Partial charges of all atoms in acetone cyanohydrin obtained from NBO calculations at the CCSD(T)/aug-cc-pVTZ level of theory. The colors represent the sign of the charge. Lighter color indicates larger magnitude of the partial charge.

However, the predominant contribution to the high methyl barrier arises the repulsive interactions of the hydrogen atoms with the remaining substituents.

4. Conclusion

The microwave spectrum of *gauche* acetone cyanohydrin is investigated using high resolution microwave spectroscopy in combination with quantum chemical calculations. Not only the nuclear quadrupole hyperfine structure was revealed, additional splittings observed for all a- and c-type transitions occur at the same order of magnitude governed by Coriolis interactions, thereby providing a unique fingerprint pattern of each rotational transition. Due to the low barrier tunneling motion of the hydrogen atom in the hydroxyl group, b-type transitions split into doublets with large separation expected to be around 100 GHz. Since the energy separating the two inversion tunneling states could not be obtained directly from an observed b-type 0^+ - 0^- splitting, we used an empirically found correlation between ΔE and V to predict a ΔE value. Additionally, we fitted the measured signals with a model Hamiltonian accounting for Coriolis coupling and related distortion

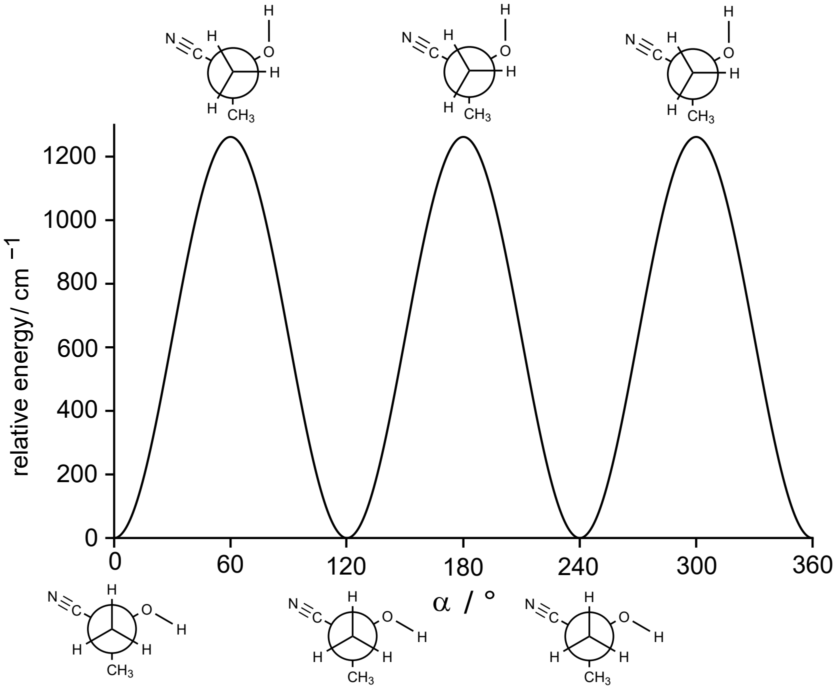


Figure 5: Calculated V_3 potential of the methyl group in the *gauche* conformer of acetone cyanohydrin at the B3LYP-D3BJ/aug-cc-pVTZ level of theory.

terms to obtain ΔE. Confidence is gained from both values being in remarkable agreement with each other. However, additional measurements in the millimeterwave region are advised to remove possible correlations from the determined spectroscopic constants resulting in an improved frequency range extrapolation for a out-of-band prediction and subsequent interstellar search.

Acetone cyanohydrin has potential for astronomical searches based on the confirmed existence of the plausible educts acetone and hydrogen cyanide in the interstellar medium along with a low-barrier possible reaction pathway.

5. Acknowledgement

We dedicate this work to Frank J. Lovas to honour his outstanding contributions to the laboratory detection of molecules with astrochemical importance as well as their detection in deep space. Remarkably, he played a role in the characterization of more than one third of all experimentally verified astrochemical species, emphasizing the great impact of his work on this field.

The authors thank the Land Niedersachsen and the Deutsche Forschungsgemeinschaft for funds. K.G.L. gratefully acknowledges the Fonds der Chemischen Industrie for a Ph.D. fellowship. H.V.L.N. was supported by the Agence Nationale de la Recherche ANR (project ID ANR-18-CE29-0011).

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