

NASA LAW, February 14-16, 2006, UNLV, Las Vegas

Difficulties in Laboratory Studies and Astronomical Observations of Organic Molecules: Hydroxyacetone and Lactic Acid

A. J. Apponi, M. A. Brewster¹, J. Hoy, & L. M. Ziurys

Life and Planets Astrobiology Center, The University of Arizona, Tucson, AZ, 85721

aapponi@as.arizona.edu

ABSTRACT

For the past 35 years, radio astronomy has revealed a rich organic chemistry in the interstellar gas, which is exceptionally complex towards active star-forming regions. New solar systems condense out of this gas and may influence the evolution of life on newly formed planets. Much of the biologically important functionality is present among the some 130 gas-phase molecules found to date, including alcohols, aldehydes, ketones, acids, amines, amides and even the simplest sugar - glycolaldehyde. Still, many unidentified interstellar radio signals remain, and their identification relies on further laboratory study.

The molecules hydroxyacetone and lactic acid are relatively small organic molecules, but possess rather complex rotational spectra owing to their high asymmetry. Hydroxyacetone is particularly problematic because it possess a very low barrier to internal rotation, and exhibits strong coupling of the free-rotor states with the overall rotation of the molecule. As in the case of acetamide, a full decomposition method was employed to order the resultant eigenstates onto normal asymmetric top eigenvectors.

1. Introduction

Over 130 molecules have now been discovered in the interstellar medium. The prevailing theme of astrochemistry is organic in nature. Most of the molecules found are hydrocarbons and their organic derivatives. There are only two places in which organic molecules are known to exist, (i) in interstellar space and (ii) in living (or once living) organisms on Earth. The question is whether there is a connection between these two regimes. It becomes more and more plausible that organic material delivered to the early Earth via meteorites and

¹Current address: SFRYI Inc., Seattle, WA, 98109

comets may have provided the necessary building blocks that facilitated the process and evolution of life.

Still, a complete chemical inventory of the interstellar medium is lacking. It is estimated that about 1/2 of the interstellar features in the millimeter and submillimeter wave region 65 to 600 GHz remain unidentified. These unidentified lines are either from highly excited states of already known molecules or from highly asymmetric carriers whose rotational frequencies still remain unknown. Although some lines from excited states of vinyl cyanide and a few other molecules have recently been assigned, many still remain even though most of the relevant excited state spectroscopy is already complete. It is therefore more likely that highly asymmetric molecules whose spectra are unknown account for the bulk of the remaining lines.

2. Rotational Spectrum of Hydroxyacetone

Of all of the stable molecules with the chemical formula $C_3H_6O_2$, hydroxyacetone is the only remaining species requiring further spectroscopy characterization. It has proven very difficult to characterize owing to its methyl rotor, which has a very low barrier to internal rotation of about 65 cm^{-1} . This low barrier allows the free-rotor states to heavily mix with the asymmetric top states to the point where K_a is no longer a good quantum number, except at low- J . We have now been able to solve this system in its ground torsional state with a fit that reproduces the measured frequencies to the measurement uncertainty.

The rotational spectrum of hydroxyacetone was first recorded by Kattija-Ari and Harmony (1980) in the microwave region. They measured a total of 43 lines both in the A and E states, where unfortunately some E-state assignments were incorrect. However, with their work, the A-state was easy to predict at other frequencies and a reasonable structure and barrier height were determined (see Table 2). Braakman et al. 2005 were able to extend the work to include 587 A-state lines at millimeter wavelengths. They also assigned, but could not fit, 288 E-state lines.

At about the same time as Braakman et al. (2005), we started to measure the rotational spectrum of hydroxyacetone using our newly built Fourier transform microwave (FTM) spectrometer and one of the Ziurys group millimeter-wave direct absorption spectrometers in the frequency range of 5 to 20 GHz and 65 to 175 GHz. In all, more than 1000 lines have been assigned to the ground state of hydroxyacetone.

The Rho-axis Hamiltonian was used for the analysis of hydroxyacetone, which couples the internal rotor to the a -axis producing an off-diagonal term in the rotational Hamiltonian

$$\hat{H}_{rot} = \frac{1}{2}(B + C)(\hat{P}_b^2 + \hat{P}_c^2) + A\hat{P}_a^2 + \frac{1}{2}(B - C)(\hat{P}_b^2 - \hat{P}_c^2) + D_{ab}(\hat{P}_a\hat{P}_b + \hat{P}_b\hat{P}_a), \quad (1)$$

and results in a torsional coupling of the form

$$\hat{H}_{tors} = F(\hat{P}_\gamma - \rho\hat{P}_a)^2 + \frac{1}{2}V_3(1 - \cos 3\gamma) + \frac{1}{2}V_6(1 - \cos 6\gamma), \quad (2)$$

where \hat{P} are the regular angular momentum operators along the respective axes and A, B, C and F are the associated rotational constants. The terms V_3 and V_6 are potential

terms associated with the internal motion of the methyl rotor. The details of the Rho-axis Hamiltonian and eigenfunction decomposition methods used here can be found in Ilyushin (2004) and the references therein.

Twenty-one rotational constants have been fit to 1045 lines covering $J < 31$ and $K_a < 8$ (see Table 1). Only the leading order terms are included here for conciseness. Both the A and E states were fit simultaneously using the rho-axis method. The E-state is very sensitive to the barrier height of the internal rotor and has been determined to high accuracy. Excited torsional lines have not yet been included in the fit.

Table 1: Leading order parameters for hydroxyacetone

Parameter	Operator	This Work	Kattija-Ari et al.
V_3	$1/2(1 - \cos 3\gamma)$	65.377(28) cm^{-1}	68(4) cm^{-1}
F	\hat{P}_γ^2	159.161(53) GHz	157.931 GHz (fixed)
ρ	$\hat{P}_\gamma \hat{P}_a$	0.058674(77) unitless	ND
A (diagonalized)	\hat{P}_a^2	10013.53(61) MHz	10069.410(57) MHz
B (diagonalized)	\hat{P}_b^2	3834.36(16) MHz	3810.412(8) MHz
C (diagonalized)	\hat{P}_c^2	2911.04(12) MHz	2864.883(4) MHz
D_{ab}	(\hat{P}_a, \hat{P}_b)	1216.18(35) MHz	ND
$\Delta I = I_c - I_a + I_b$		8.7 $\text{amu}\text{\AA}^2$	6.4 $\text{amu}\text{\AA}^2$
Total Number of Lines		1045	53
Microwave rms		6 kHz	A-state 20 kHz
Millimeter wave rms		70 kHz	E-state 9 MHz

3. Astronomical Searches

We have now been able to search for both hydroxyacetone and lactic acid in the Sgr B2(N) molecular cloud. The millimeter wave spectrum of Lactic acid was recently published by Psczolkowski et al. (2005). The barrier height of methyl rotation is predicted to be around 1100 cm^{-1} ; however, the coupling of the internal motion to the rigid frame is not strong enough to produce a resolved E-state for lactic acid. This is unfortunate because it would effectively double the number of possible lines; hence, there would be less chance of confusion by contamination in the space spectrum.

Even though we have found a number of coincidental matches for both of these species, there are too many missing transitions for a definitive identification of either molecule. The frequencies that show ‘holes’ in the spectra of these molecules lie in very confused regions often times straddled by larger features. These searches yield upper limits to the column densities of $< 5 \times 10^{13} \text{ cm}^{-2}$ for hydroxyacetone and $< 9 \times 10^{13} \text{ cm}^{-2}$ for lactic acid. These upper limits can be used in chemical modeling. Some representative spectra are shown in Figure 1.

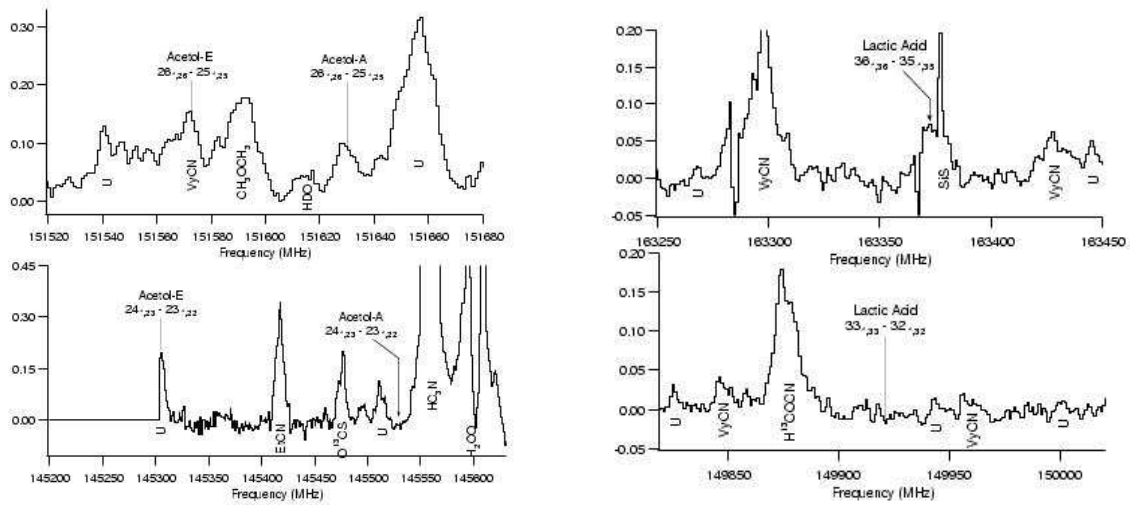


Fig. 1.— Representative astronomical spectra of hydroxyacetone and lactic acid towards Sgr B2(N). These spectra show that even though there are several coincidental matches for these molecules, the absence of features at several favorable transitions indicates that they are not abundant enough for detection.

This material is based upon the work supported by the National Aeronautical and Space Administration through the NASA Astrobiology Institute under cooperative agreement No. CAN-02-OSS-02 issued through the office of Space Science. We would also like to thank Isabella Kleiner for sharing her Hamiltonian computer program.

REFERENCES

- Braakman et al. 2005, 60th Int. Symp. Mol. Spectr., Ohio State University
 Halfen et al. 2006, ApJ, 639, 237
 Hollis et al. 2000, ApJ, 540, L107
 Ilyushin 2004, J. Mol. Spectr., 227, 140
 Kattija-Ari and Harmony 1980, Int. J. Quan. Chem., 14, 443
 Pszczokowski et al. 2005, J. Mol. Spectr., 234, 106