Millimeter-wave Rotational Spectroscopy of Pyridine (C_5H_5N), Pyridazine ($C_4H_4N_2$), and Their Discharge Products with efforts toward Phenyl Radical (C_6H_5), *ortho*-Benzyne (*o*-C_6H_4), Protonated Benzene ($C_6H_7^+$)

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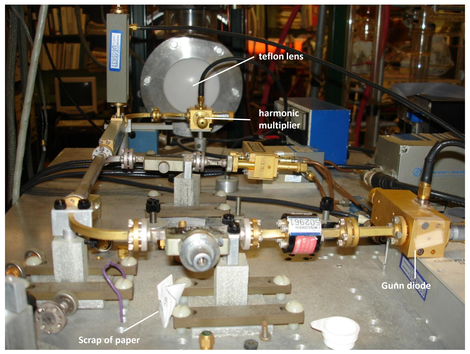
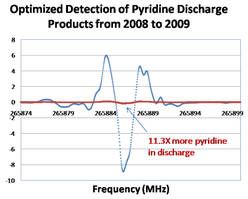


Millimeter wave Spectrometer

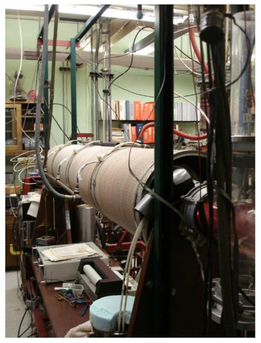
- 3 meter-Pyrex discharge chamber (10 cm diameter)
- Gunn-diode microwave signal source with harmonic multiplier
- LN2, water, or CFC-135 cooled discharge chamber
- Liquid helium cooled 1.7 K indium-antimonide detector
- DC glow discharge with hollow cylinder electrodes
- Water cooled magnetic coil
- "Leaky garden hose" apparatus for even reactive gas distribution
- Quadrupole mass spectrometer

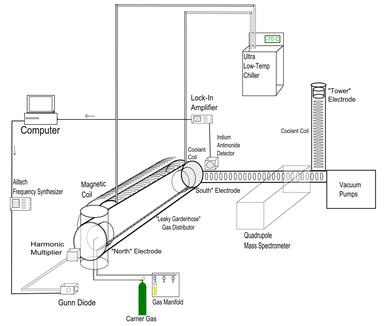
Petrmichl, R. H. Thesis, University of Wisconsin, 1990

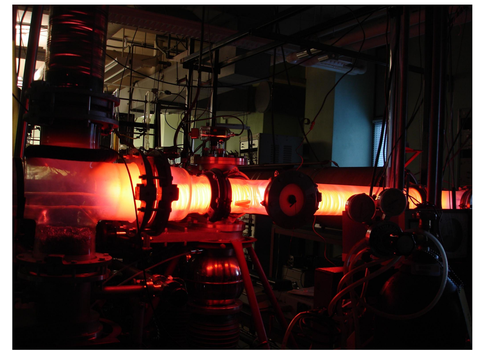


2009 (blue line) improvement based upon

- Garden hose
- Improved temperature control
- Improved tuning
- Improved discharge conditions

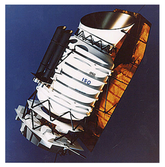


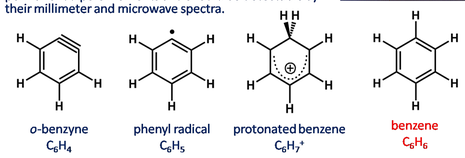




The Search for Benzene Derivatives in the ISM

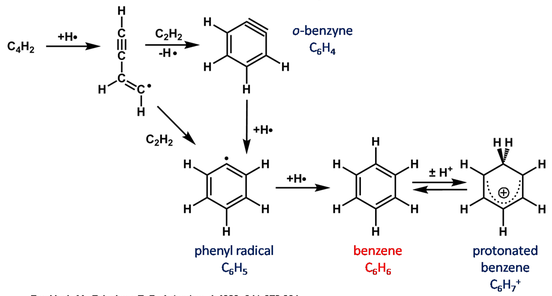
- Benzene detection was reported in proto-planetary nebula CRL 618 using infrared spectroscopy via the Infrared Space Observatory.
- Benzene, due to its symmetry and resulting lack of a dipole moment, does not exhibit pure rotational transitions.
- Fortunately, several closely related species do have permanent dipole moments and should be detectable by their millimeter and microwave spectra.





Cernicharo, J.; Heras, A. M.; Tielens, A.; Pardo, J. R.; Herpin, F.; Guelin, M.; Waters, L. *Astrophys. J.* **2001**, *546*, L123-L126.

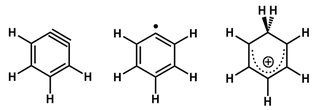
Proposed Chemistry of Benzene in Proto-Planetary Nebula



Frenklach, M.; Feigelson, E. D. *Astrophys. J.* **1989**, *341*, 372-384.

Previous Work with Benzene Derivatives

Green Bank Telescope

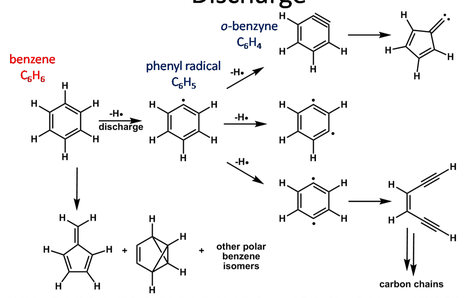


μ = 1.4 D μ = 0.9 D μ = 0.8 D

- Previously, Weaver et al (2007) searched unsuccessfully using the GBT for *o*-benzyne in the PPN CRL 618 using predicted millimeter-wave rotational transitions.
- Experimental rotational transitions are available for phenyl radical in the microwave and theoretical rotational transitions are available in the millimeter region. *O*-benzyne has been observed in the microwave region.

Weaver, S. L. W.; Remijan, A. J.; McMahon, R. J.; McCall, B. J. *Astrophys. J. Lett.* **2007**, *671*, L153-L156.
McMahon, R. J.; McCarthy, M. C.; Gottlieb, C. A.; Dudek, J. B.; Stanton, J. F.; Thaddeus, P. *Astrophys. J.* **2003**, *590*, L61-L64.

Proposed Chemistry of Benzene in a Discharge

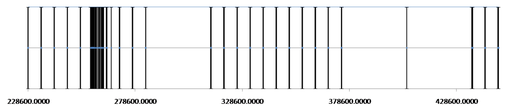


McMahon, R. J.; McCarthy, M. C.; Gottlieb, C. A.; Dudek, J. B.; Stanton, J. F.; Thaddeus, P. *Astrophys. J.* **2003**, *590*, L61-L64.

Pyridazine Millimeter-wave Observations

- Based upon the microwave work of Werner et al, we predicted and observed more than 200 transitions between 228 and 448 GHz.
- Pyridazine had a lower than expected volatility and observed pressures < 1 mtorr.
- Strong bands of transitions are separated by approximately 2C ≈ 6100 MHz with the strongest signal from $J=X_{0,X}$ -> $J=X\text{-}1_{0,X\text{-}1}$.

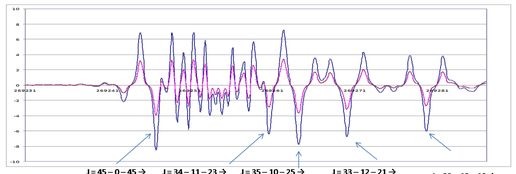
Assigned Transistions of Pyridzaine from 228600 MHz to 428600 MHz



Werner, W.; Dreizler, H.; Rudolph, H. D. Z. Naturforsch.,A: Phys. Sci. **1967**, *A 22*, 531-543.

Pyridine Detection

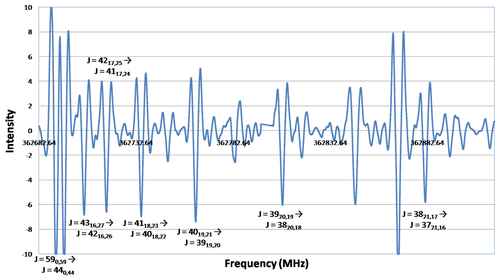
- Pyridine, another aromatic compound, may serve as a good analog for the behavior of benzene in a discharge. The advantage of pyridine is that it possesses a strong permanent dipole moment, allowing for the easy detection of our starting material.
- Shown here is the ability of pyridine to persist in a discharge. The following transitions were observed using at 1 mTorr pyridine and 16 mTorr of argon. The blue trace is without discharge, and the pink trace is when a 1500 V, 5 mA negative glow discharge is applied.



Ye, E., Bettens, R. P. A., De Lucia, F. C., Petkie, D. T., Albert, S. 2005, J. Mol. Spectrosc., 232, 61.

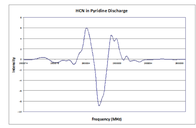
Representative Transitions in our Pyridazine Spectrum

Pyridazine < 1 mtorr at ≈ 290 K from 362682 MHz to 362918 MHz



Products of Pyridine Discharge

H—C≡N
hydrogen cyanide

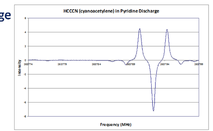


J = 3 → J = 2 265886.322 MHz

-Negative glow discharge
1500 V / 5 mA

-1 mTorr Pyridine
-1 mTorr H_2
-1 mTorr Ar

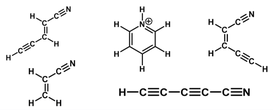
H—C≡C—C≡N
cyanoacetylene



J = 29 → J = 28 263792.331 MHz

J = 3 → J = 2 259011.78 MHz

Other possible products to look for in a pyridine discharge



H—C≡C—C≡C—C≡N

Products of Pyridine Discharge

J = 3 → J = 2 265886.322 MHz

-Negative glow discharge
1500 V / 5 mA

-1 mTorr Pyridine
-1 mTorr H_2
-1 mTorr Ar

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Other possible products to look for in a pyridine discharge

H—C≡C—C≡C—C≡N

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Special Thanks to
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