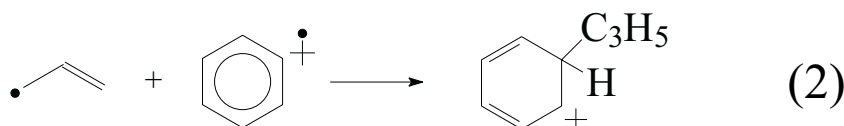
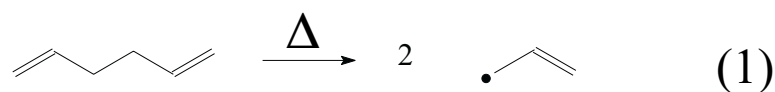


## **Introduction:**

- We are interested in the reactions of gas-phase ions with reactive intermediates such as radicals.
- Reactive species pose a problem since they are short-lived, difficult to make, and often dangerous to handle.
- Reactions of radicals in a mass spectrometer can be conducted by using distonic ions having stable charge sites as the radical reactant [1].
- The approach of interest to us is pyrolysis of suitable precursors possessing a weak bond, leading to beams of unstable species, which can be seeded in a supersonic beam of inert carrier gas [2,3].
- In this poster, we describe the coupling of a pyrolysis nozzle, based on the work of Chen [3], with an FT-ICR. Although supersonic beams have been used previously with FT-ICRs [5], this is the first attempt to couple a pyrolysis jet for generating radicals for reaction with gas-phase ions.

## The Model Reaction:

We have chosen the reaction of allyl radical, which can be generated by pyrolysis of 1,5-hexadiene (reaction1), with benzene radical cation (reaction2) to demonstrate feasibility.



To test the reactivity of the radical with the cation, we calculated, using PM3, an energy profile for the reaction 2 (Fig. 1) and compared it with the profile for reaction of the radical with neutral benzene (Fig. 2).

The reaction of the radical cation and radical should be rapid and without activation energy, unlike that of the radical and neutral benzene.

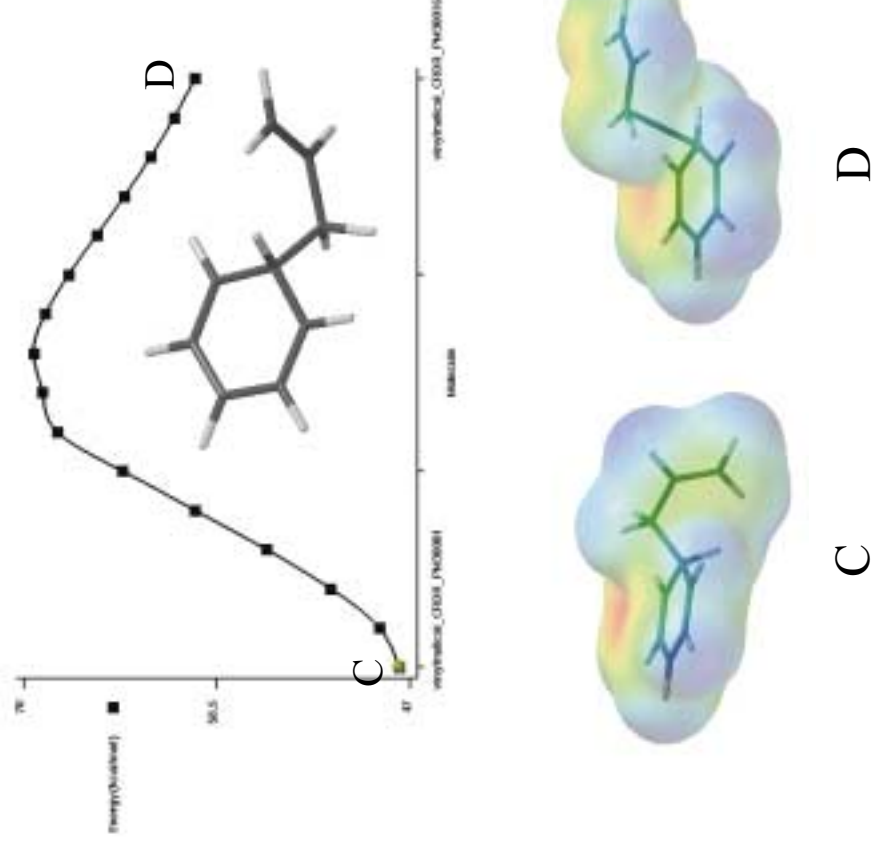
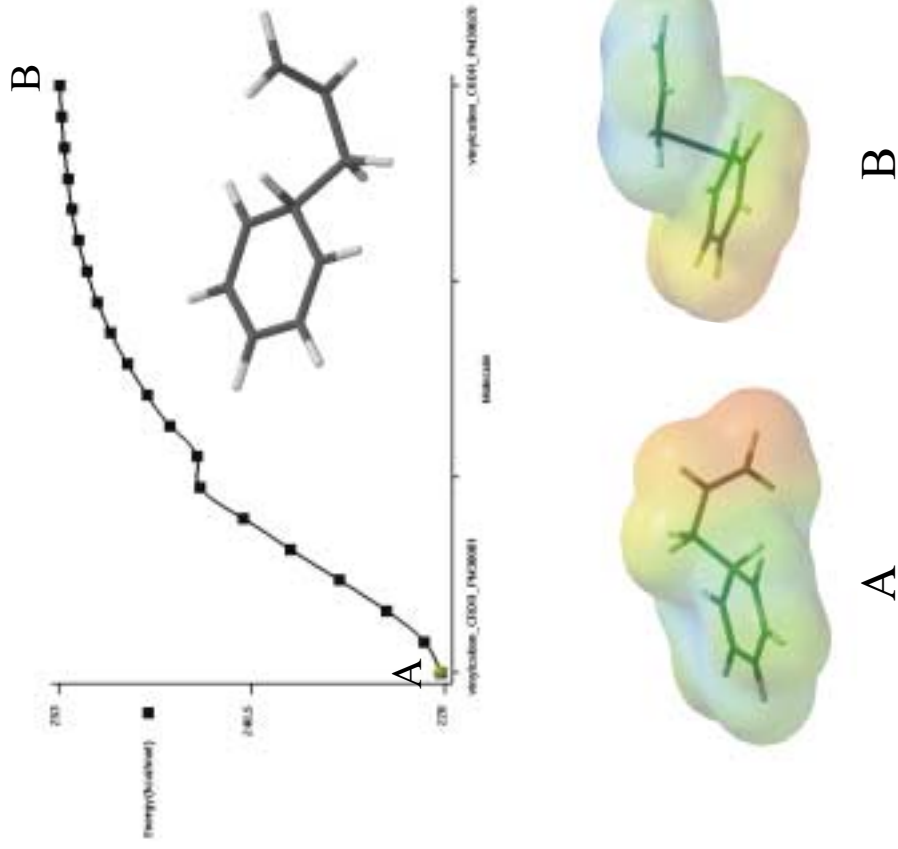


Figure 1

Figure 2

## Instrumentation:

An FT-ICR spectrometer has been modified to accommodate a pulsed nozzle, which serves as the radical source. A modified trap serves as the chamber for the reactions of radical and ions.

## Description of FT-ICR:

The spectrometer is equipped with:

### *Pulsed Valve*

The pulsing of the valve is interfaced to the experimental sequence generated by the FTMS 1280 software (Fig. 3).

### *Modified 2" ICR cell*

The original cell was equipped with new detection plates that were made with 67% transmitting stainless steel mesh. This is necessary for the supersonic beam has to move through the cell.

### *1.2 Tesla magnet (Varian)*

### *Vacuum system*

The vacuum system consists of a custom chamber pumped by a 500 L/s turbo molecular pump (Balzers TPU500) backed by a two stage roughing pump (Welch 1397).

The chamber is equipped with the new pulsed valve as well as ports for a desorption probe, a laser beam, and a gas inlet system.

### *Nicolet FTMS 1280 data system*

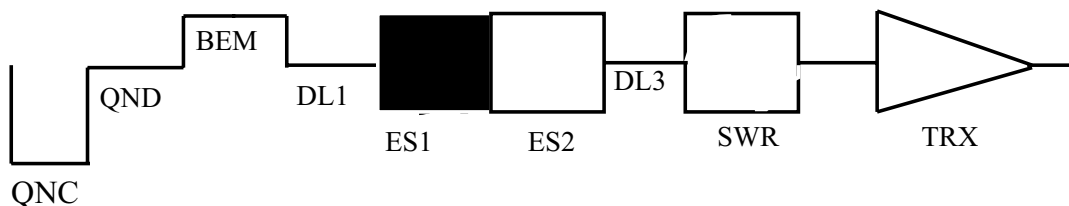


Figure 3: Typical FT-ICR Sequence

## Description of the Pyrolysis Nozzle

- Pyrolysis nozzle, based on design by Chen [2,3], employs a 0.040" I.D., 0.020" wall thickness silicon carbide tube (Hexoloy SA, Carorundum, Niaagra Falls, NY).
- SiC tube is nested and cemented with ceramic adhesive (903HP, Cotronics, Brooklyn, NY) in a standard aluminum oxide tube. The aluminum oxide tube also cemented into the nickel seat (See Fig. 4).
- Tube heated resistively until  $\sim 1850$  K.
- Seeded beam intersects a small cloud of ions undergoing cyclotron motion inside ICR cell.
- High-speed gas flow is needed for short residence times inside nozzle and for creating a directional beam in vacuum chamber.

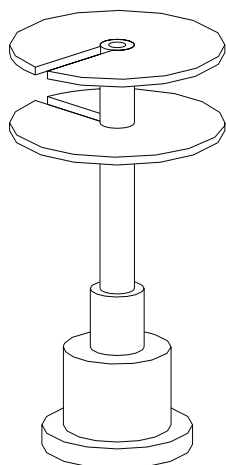
## Advantages of ICR/Pyrolysis Nozzle Combination

- ICR is highly sensitive, unlike other spectroscopic techniques [4].
- Large quantities of dangerous precursors not needed.
- Ions of  $m/z$  1000 in the cell with a radius of 1 cm are traveling at  $\sim$  the same velocities as neutrals in the seeded beam ( $\sim 10^3$  m/s).
- Gentle reactions (e.g., charge exchange) if ions and the neutral beam are moving in same direction.
- Trapped products of ion-radical reactions can be studied since the detection in an FT-ICR is nondestructive.
- Ionized radicals could be stored for subsequent studies of their reactivity.

# Schematic of Pyrolysis Nozzle

<u>Voltage (V)</u>	<u>Current (A)</u>	<u>Ballast (W)</u>	<u>Temp. (C)</u>
21.2	0.50	100	700
19.0	1.05	150	953
20.3	1.39	200	1108
24.3	2.00	100+200	1375
23.8	2.89	150+200	1536

Ballast resistance (light bulbs) were parallel when two were used.

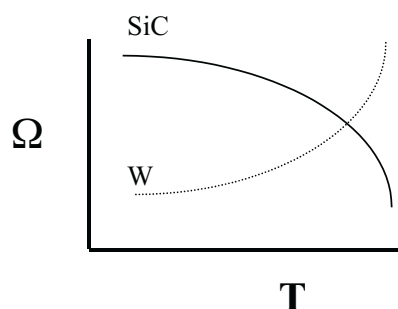


Graphite Contacts

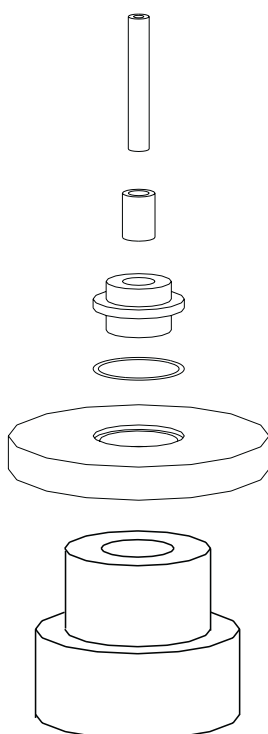
Silicon Carbide Nozzle

Alumina Insulator

Nickel Base



## Exploded View of Nozzle



SiC Nozzle

Alumina Insulator

Nickel Seat

Gold O-Ring

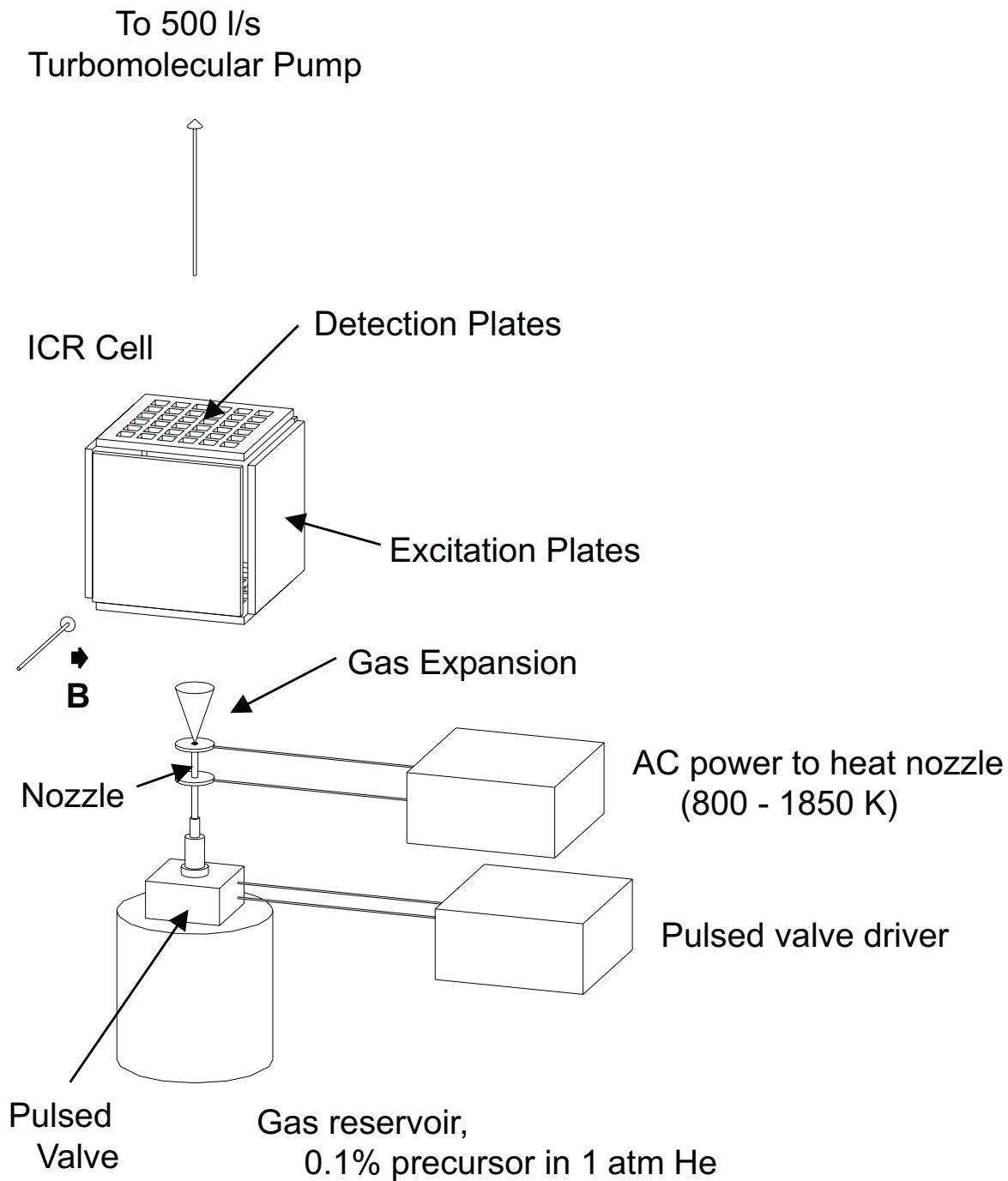
SS O-Ring Seat

General Valve

The precursors spend several microseconds in the hot-wall reactor where they are pyrolyzed to give radicals that expand into the vacuum. This technique is capable of making radicals at high density,  $\sim 10^{14} \text{ cm}^{-3}$

Figure 4

# Schematic of FT-ICR and Pyrolysis Jet



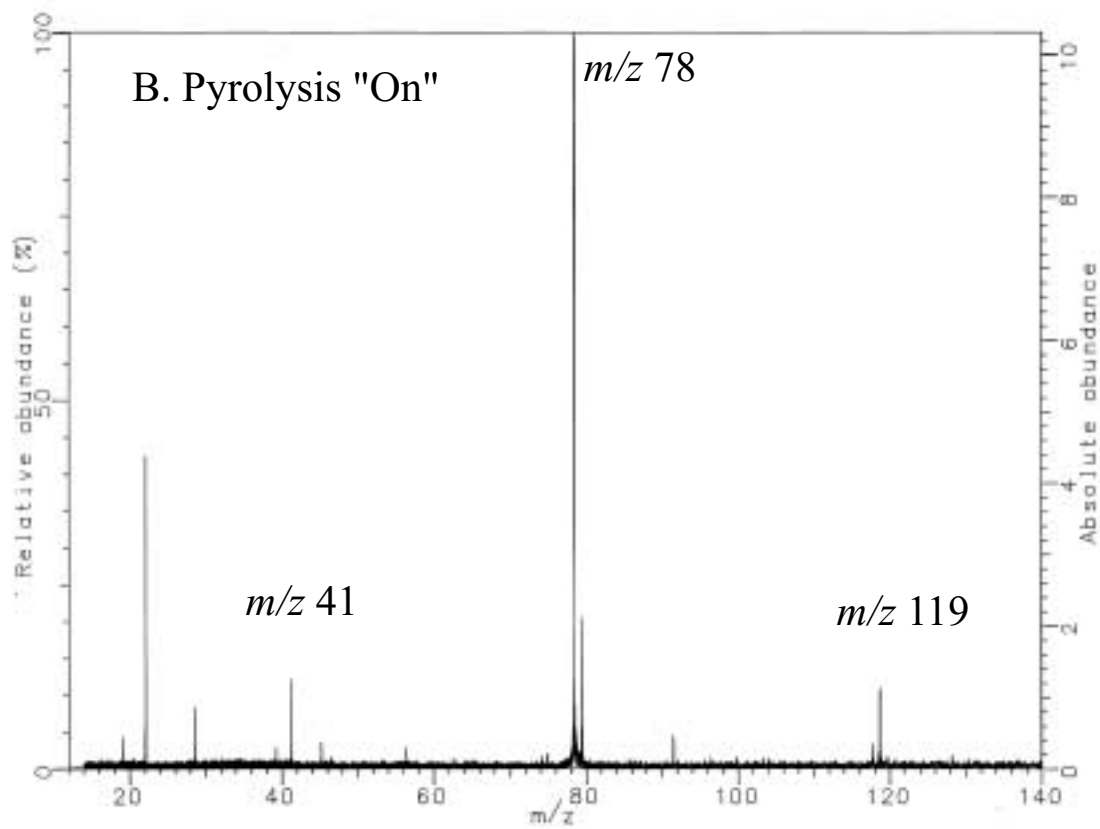
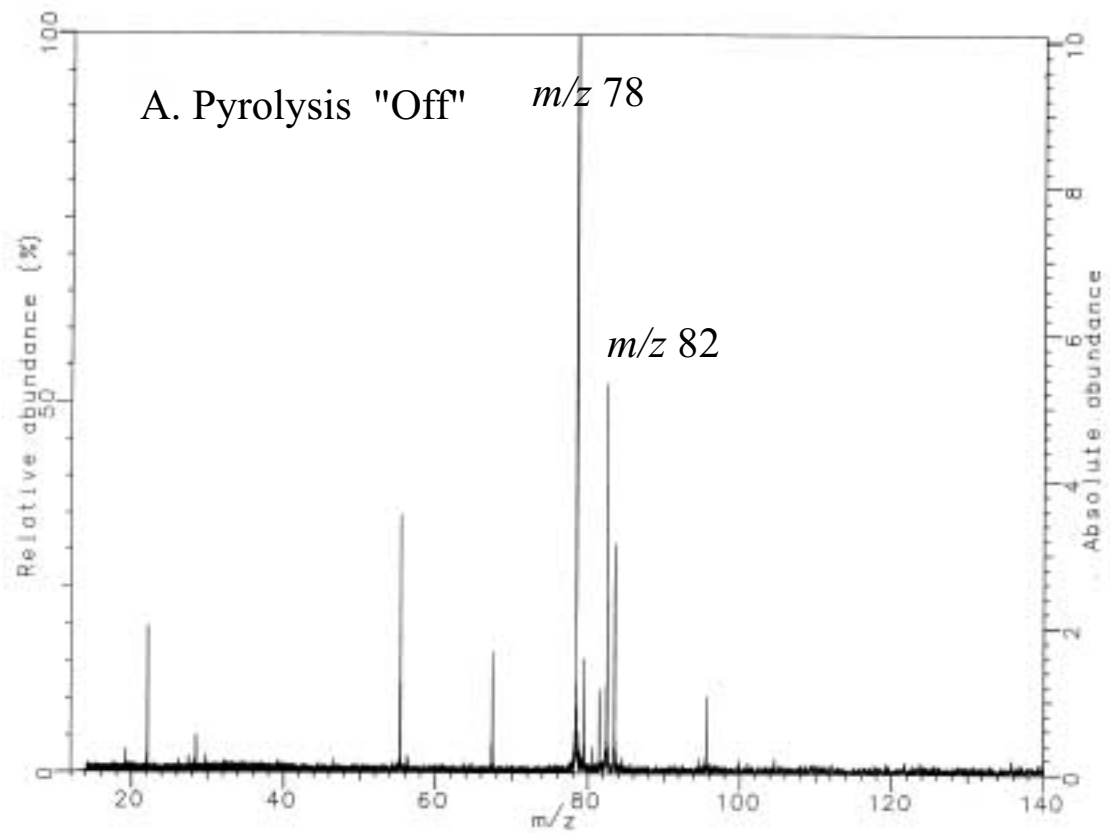


Figure 5

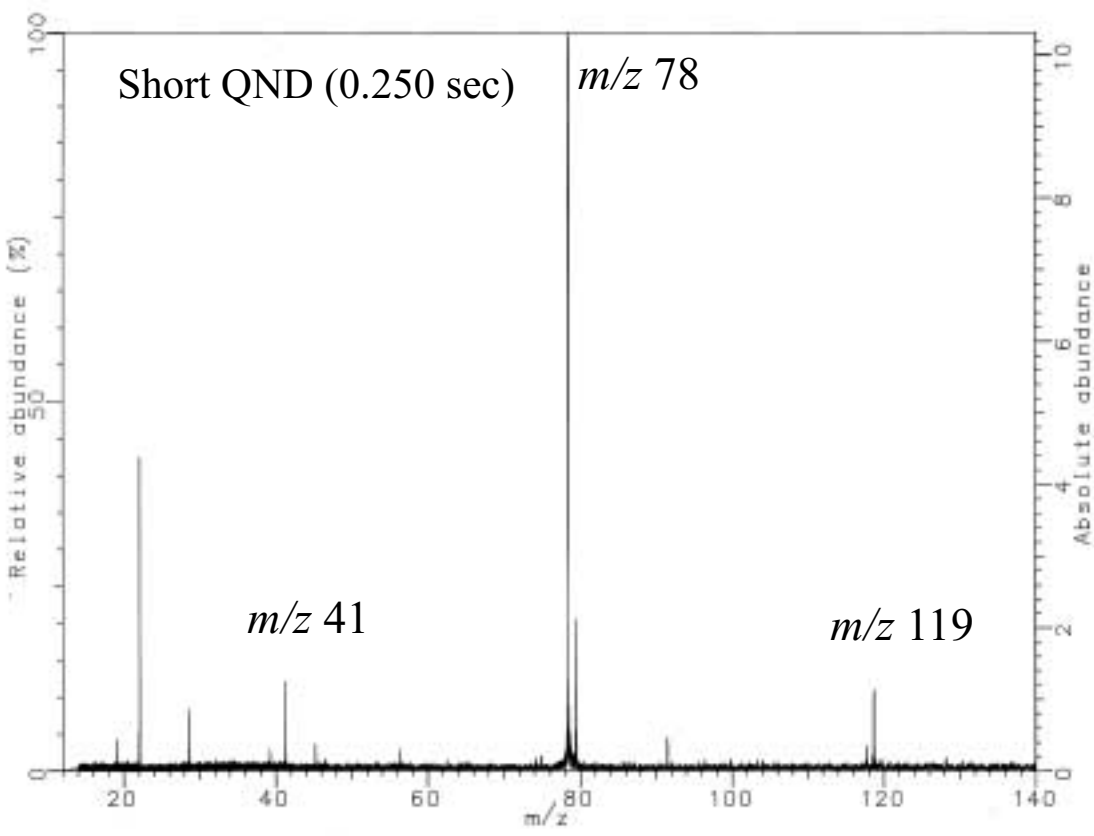
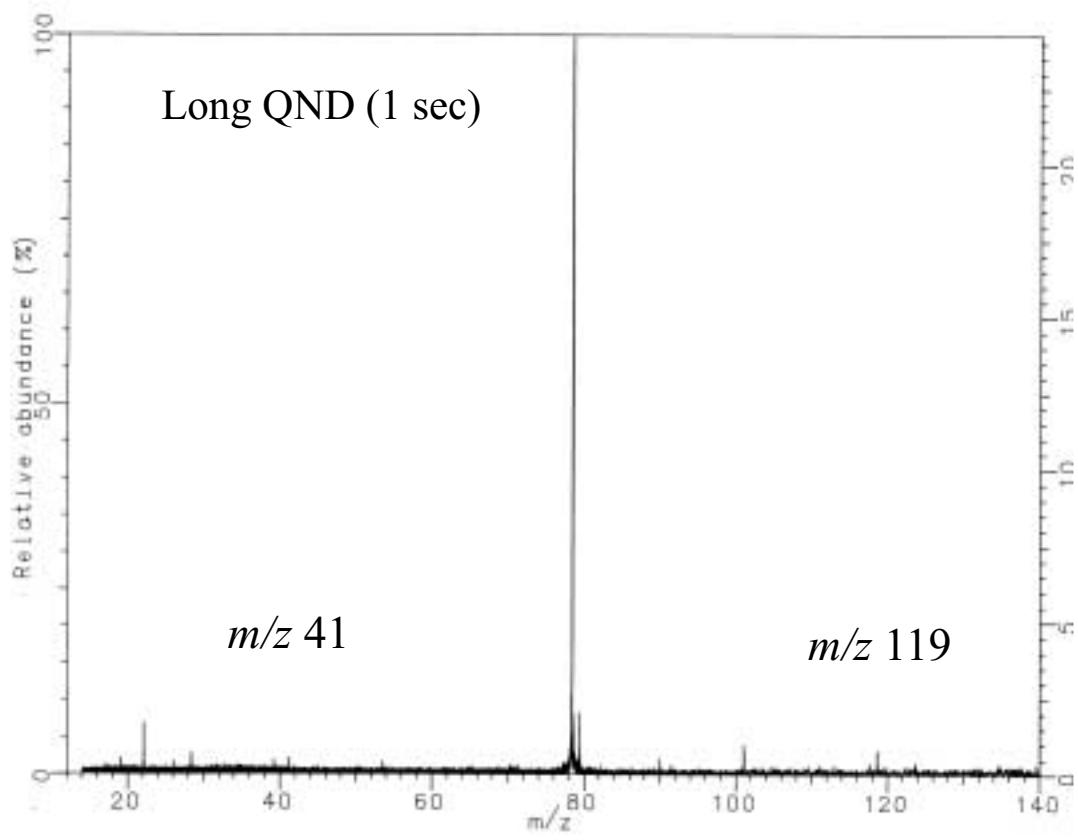


Figure 6

## Results: Reaction of Allyl Radical with Benzene Radical Cation:

The allyl radical was generated in the pyrolysis nozzle (see reaction 1) and pulsed into the ICR trap containing stored benzene radical cations. The radical cations were formed by EI of benzene held at a background pressure of  $\sim 2 \times 10^{-7}$  torr. All ions other than  $m/z$  78 were ejected prior to the nozzle pulse (DL3 in Fig 3).

Following the nozzle pulse is a delay of  $\sim 500$  ms to allow reaction to occur. Product ions are then excited and detected as usual.

In the first experiment (Fig. 5A), the nozzle is pulsed but not heated. The mass spectrum shows the 1,5-hexadiene radical cation of  $m/z$  82 (formed by charge exchange with benzene radical cations) and unreacted benzene radical cation. In the second experiment (Fig. 5B), the nozzle is pulsed and heated, producing neutral allyl radical, which charge exchanged to  $m/z$  41 ions, and which react with benzene radical cation to give  $C_6H_6-C_3H_5^+$  at  $m/z$  119 (see reaction 2).

The effect of third body collisions on the extent of reaction 2 and on the charge exchange is shown in Figure 6. The effect of shortening the QND delay is that more He from the previous nozzle pulse is remaining in the trap, thereby, increasing the probability of a second collision leading to more stabilized adduct (Fig. 7).

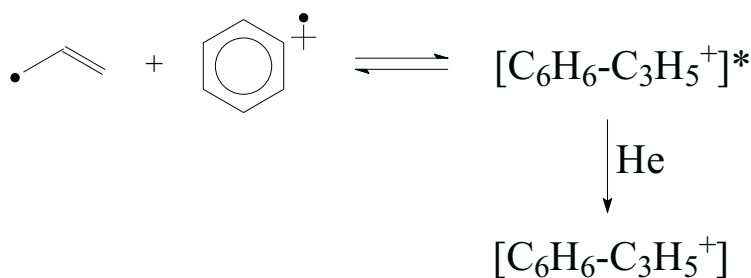


Figure 7

## **Conclusions:**

- A pulsed pyrolysis nozzle that can achieve 1 ms pulse widths and temperatures up to 1850 K has been interfaced to an FT-ICR modified trap.
- Reactions between benzene radical cation and the vinyl radical beam have been observed for the first time.

## **Future Plans:**

- Modify experiment based on first-round results:
  - Shorter radical Pulses
  - He pulse for a localized high pressure event
  - Introduction of an RF only mode event
- Decompose a variety of novel compounds to generate singlet and triplet silylenes
- Create an experiment to probe ion interactions with a wide variety of reactive intermediates. Subject ions will ultimately be biomolecule species (peptides, oligonucleotides).

## **References:**

1. See, for example, K. M. Stirk, L. K. Kiminkinen, H. I. Kenttamaa *Chem. Rev.* **7** 1649-1665 (1992) and S. J. Yu, C. L. Holliman, D. L. Rempel, and M. L. Gross *J. Am. Chem. Soc.* **21** 9676-9682 (1993).
2. J. A. Blush, H. Clauberg, D. W. Kohn, D. W. Minsek, X. Zhang, and P. Chen *Acc. Chem. Res.* **25** 385-392 (1992).
3. D. W. Kohn, H. Clauberg, and P. Chen *Rev. Sci. Instrum.* **63** 4003-4005 (1992).
4. H. W. Rohrs, C. T. Wickham-Jones, G. B. Ellison, D. Berry, and B. M. Argrow *Rev. Sci. Instrum.* **66** 2430-2441(1995).
5. J. J. Elkind, J. M. Alford, F. D. Weiss, R. T. Laaksonen, and R. E. Smalley *J. Chem. Phys.* **87** 2397-2399 (1987).
6. J. D. Anderson Modern Compressible Flow (1990) McGraw Hill.
7. D. R. Miller in G. Scoles ed. Atomic and Molecular Beam Methods 14-53 (1988) Oxford University Press.
8. D. L. Rempel and M. L. Gross *J. Am. Soc. Mass Spectrom.* **3** 590-594 (1992).

## **Acknowledgments:**

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