



# Hydrogen Abstraction/Acetylene Addition Revealed

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# INTRODUCTION

For almost half a century, polycyclic aromatic hydrocarbons (PAHs) have been proposed to play a key role in the astrochemical evolution of the interstellar medium (ISM) and in the chemistry of combustion systems.

In recent decades, electronic structure calculations and kinetic models proposed the hydrogen abstraction–acetylene addition (HACA) mechanism to dominate the formation of PAHs in combustion flames and in the interstellar medium.

However, even the most fundamental reaction mechanism assumed to lead to the simplest PAH naphthalene has eluded experimental observation.

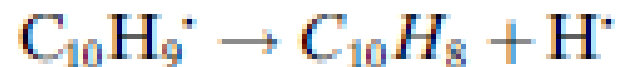
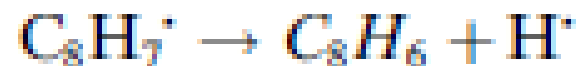
Here, by probing the phenylacetylene ( $C_8H_6$ ) intermediate together with naphthalene ( $C_{10}H_8$ ) under combustion-like conditions by photo-ionization mass spectrometry, the very first direct experimental evidence for the validity of the HACA mechanism is reported.

HACA mechanism implies a repetitive reaction sequence of an abstraction of a hydrogen atom from the reacting aromatic hydrocarbon (AH) by a hydrogen atom followed by addition of an acetylene molecule (C<sub>2</sub>H<sub>2</sub>) to the radical site with A being an aromatic species.



Starting from benzene ( $C_6H_6$ ), this mechanism lead first to the phenyl radical ( $C_6H_5$ ) followed by addition of an acetylene molecule ( $C_2H_2$ ) forming the styrenyl radical ( $C_8H_7$ ).

The second step of the HACA mechanism, a subsequent acetylene addition to the ortho-vinylphenyl radical ( $C_8H_7$ ) or hydrogen abstraction from the phenylacetylene molecule ( $C_8H_6$ ) followed by addition of another acetylene molecule ( $C_2H_2$ ) ultimately yields naphthalene ( $C_{10}H_8$ ) by cyclization and hydrogen abstraction at elevated temperatures of up to 1000 K.



However, despite the popularity of the HACA mechanism, it has not been observed experimentally.

Flame models are plagued by an overwhelming number of possible reaction pathways, and it is complicated to truly ascertain from which reactants distinct PAHs are formed.

Therefore, mechanistic routes to PAH synthesis have remained conjectural, and the formation mechanisms of even the simplest PAH naphthalene ( $C_{10}H_8$ ) by the HACA mechanism has not been experimentally corroborated.

Here, by exploiting the unique advantage of fragment-free photoionization by tunable vacuum ultraviolet (VUV) light and detection of the ionized molecules via a reflectron time of flight mass spectrometer (ReTOF), they are able to identify the isomer specific reaction products of the HACA mechanism and rationalize the reaction mechanism.

# EXPERIMENTAL

Here, a continuous beam of phenyl radicals ( $C_6H_5$ ) was generated in situ by quantitative pyrolysis of nitrosobenzene ( $C_6H_5NO$ ).

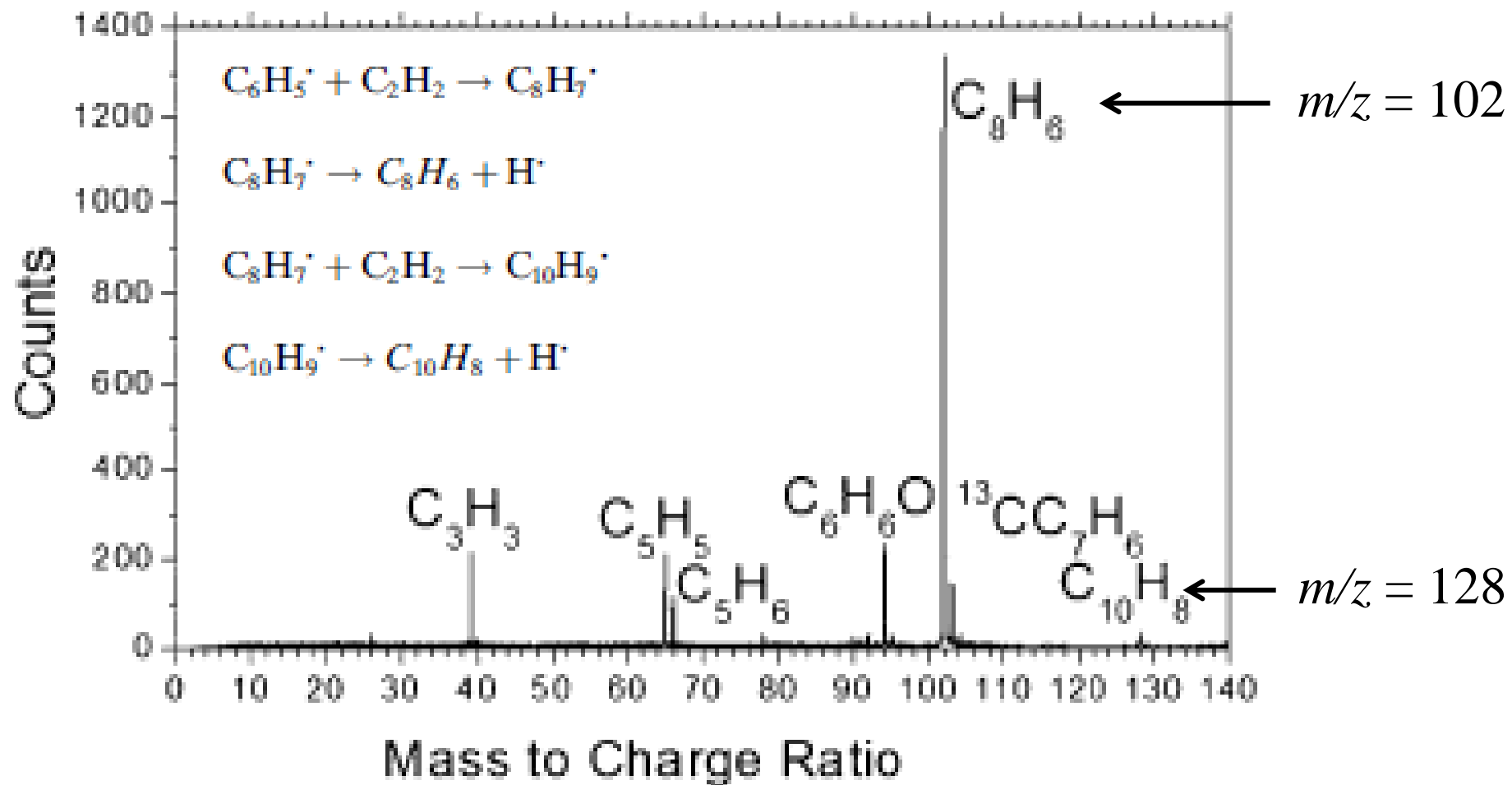
The latter was seeded in neat acetylene ( $C_2H_2$ ), which was expanded at a pressure of 300 Torr into a resistively heated silicon carbide tube at a temperature of  $1020 \pm 100$  K.

The neutral molecular beam were interrogated by quasi continuous tunable vacuum ultraviolet (VUV) radiation in the extraction region of a ReTOF mass spectrometer.

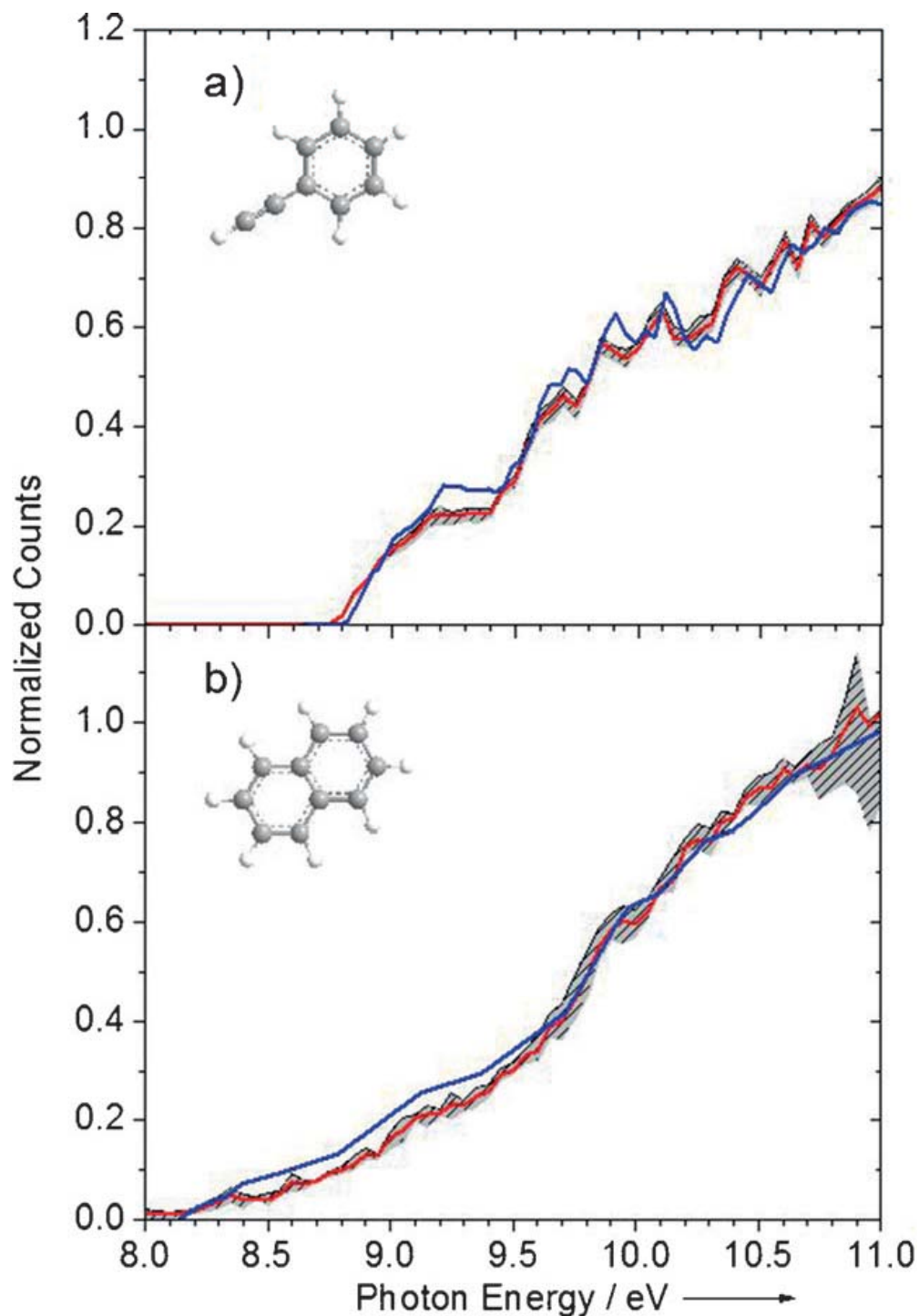
The photoionized molecules were then collected by a microchannel plate (MCP) detector.

A mass spectrum was obtained at intervals of 0.025 eV between 8.0 and 11.0 eV.

# RESULTS AND DISCUSSION



Mass spectrum of the products of the reaction of phenyl radicals with acetylene in the chemical reactor recorded at a photon energy of 9.0 eV.



Photoionization efficiency curves (PIE) recorded at  $m/z = 102$  and  $128$  shown as red lines along with experimental errors defined as the hatched grey area. The blue lines show the PIE curves for experimentally determined a) phenylacetylene and theoretically for b) naphthalene.

PIE curve of azulene ( $C_{10}H_8$ ) cannot reproduce the experimental data since the onset of the PIE arises at 7.42 eV, which is 0.72 eV lower in energy.



The signal at  $m/z = 94$  corresponds to phenol ( $C_6H_6O$ ) arising from the reaction of the phenyl radical with traces of oxygen, which produces the phenoxy ( $C_6H_5O$ ) radical followed by hydrogen abstraction.

The small signal at  $m/z = 78$  is attributed to benzene and fulvene likely formed through hydrogen atom addition (and successive isomerization) to the phenyl radical.

The resonantly stabilized free radicals propargyl ( $m/z = 39, C_3H_3$ ) and cyclopentadienyl ( $m/z = 65, C_5H_5$ ) as well as cyclopentadiene ( $m/z = 66, C_5H_6$ ) were observed also.

Recent computational investigations suggest that cyclopentadienyl radicals ( $C_5H_5$ ) might be formed through sequential hydrogen atom additions to naphthalene or as a result of phenol degradation by hydrogen atom loss to the phenoxy radical followed by carbon monoxide emission (CO) yielding the cyclopentadienyl radical.

The cyclopentadiene ( $C_5H_6$ ) and benzene molecules ( $C_6H_6$ ) can be formed through hydrogen atom addition to their aromatic radicals cyclopentadienyl and phenyl, respectively.

Once cyclopentadienyl radicals are formed they are expected to further decompose to the propargyl radical and acetylene as demonstrated in shock tube studies and theoretical investigations.

The temperature of  $1020 \pm 100$  K within the chemical reactor is high enough to overcome the reaction barriers to cyclopentadienyl and propargyl formation.

The detection of naphthalene together with phenylacetylene successfully demonstrate reaction pathways corresponding to the HACA mechanism as proposed by Frenklach and through the Bittner–Howard route.

Here, the phenyl radical ( $C_6H_5$ ) reacts with acetylene to form phenylacetylene through an acetylene versus hydrogen atom exchange pathway.

This finding correlates with a study under single collision conditions using crossed molecular beams of phenyl radicals and acetylene, which identified phenylacetylene as the reaction product formed by atomic hydrogen emission.

Here, phenylacetylene is formed through the barrier-less addition of the phenyl radical to the  $\pi$ -electron density of the carbon–carbon triple bond of acetylene yielding a  $C_8H_7$  reaction intermediate. The  $C_8H_7$  intermediate eventually decomposes by atomic hydrogen emission to phenylacetylene.

In contrast to crossed molecular beams experiments, which are conducted under single collision conditions, collisional stabilization is possible in this chemical reactor.

There can be three HACA routes possible.

Firstly, the Bittner–Howard pathway is initiated through addition of the phenyl radical to the acetylene molecule to yield the collision complex  $C_8H_7$ ; an addition of a second acetylene molecule onto the acetyl chain forms a  $C_{10}H_9$  intermediate. The C4 chain with the radical located on the terminal carbon cyclizes via radical addition to the phenyl ring and subsequent hydrogen elimination yields naphthalene.

Secondly, Frenklach's route involves shifting the radical center of the  $C_8H_7$  intermediate to the phenyl ring by hydrogen migration. A second acetylene addition to the  $C_8H_7$  aromatic radical intermediate forms a disubstituted  $C_{10}H_9$  intermediate; cyclization and hydrogen atom emission leads to naphthalene.

The third route, and original HACA mechanism proposed by Frenklach involves first the formation of phenylacetylene, followed by hydrogen abstraction from the phenyl ring to form a  $C_8H_5$  intermediate. A subsequent addition of acetylene to the ring forms a disubstituted  $C_{10}H_7$  intermediate, cyclization of the radical acetyl group forms a naphthyl radical ( $C_{10}H_7$ ) to which atomic hydrogen can be added to reach naphthalene.

Based on the calculated rate constants and barrier heights there is no preferential route discernible between the three routes.

However, from the experiment the last reaction route can be ruled out.

If the reaction proceeded with a second hydrogen atom abstraction from phenylacetylene, there should be products from acetylene addition to the meta and para positions of the aromatic ring which would not cyclize to naphthalene, and therefore change the PIE curves.

Additions to the meta and para positions would also likely result in a spread of products with different  $m/z$  ratios such as  $C_{10}H_6$  ( $m/z = 126$ ) and  $C_{10}H_{10}$  ( $m/z = 130$ ), which are not detected.

Considering that only naphthalene ( $m/z = 128$ ) was observed, it can be rationalized that the reaction mechanism proceeds through a second acetylene addition to a  $C_8H_7$  radical intermediate, either by the Frenklach or Bittner–Howard routes.

# FUTURE POSSIBILITIES

Reaction mechanism study of bigger PAHs.

Origin of heterocyclic compounds in interstellar medium.

Other fundamental reaction mechanism with help of PIE curves.

**THANK YOU**