# COMMUNICATIONS

# Crossed beams reaction of atomic carbon, C($^3P_j$), with $d_6$-benzene, C$_6$D$_6$($X^1A_{1g}$): Observation of the per-deutero-1,2-didehydro-cycloheptatrienyl radical, C$_7$D$_5$($X^2B_2$)

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The reaction of atomic carbon, C($^3P_j$) with per-deutero benzene, C$_6$D$_6$ is investigated at an average collision energy of 32.1 kJ mol$^{-1}$ using the crossed molecular beams technique combined with a universal mass spectrometric detector. Product angular distributions and time-of-flight spectra of C$_7$D$_5$ and C$_7$D$_6$ are recorded. Forward-convolution fitting of our time-of-flight data (TOFs) and laboratory angular distribution (LAB) together with high level electronic structure calculations on the singlet and triplet C$_7$D$_6$ potential energy surfaces are consistent with the formation of the per-deutero-1,2-didehydrocycloheptatrienyl radical, C$_7$D$_5$. No C$_7$D$_6$ adduct is found experimentally. Our investigations indicate that the carbon atom attacks the benzene molecule face without an entrance barrier to form an initial complex. This undergoes a ring opening to give triplet cycloheptatrienylidene as a C$_7$D$_6$ intermediate. The latter fragments without exit barrier via a C–D bond rupture to yield the per-deutero-1,2-didehydrocycloheptatrienyl isomer, C$_7$D$_5$, and a D atom. This barrierless route for the destruction of benzene may be involved in the synthesis of higher cyclic hydrocarbon derivatives in the interstellar medium, in outflows of dying carbon stars, in hydrocarbon-rich planetary atmospheres, as well as in oxygen-poor combustion flames. © *1999 American Institute of Physics.* [S0021-9606(99)01513-5]

## I. INTRODUCTION

The chemical dynamics to form (polycyclic) aromatic hydrocarbons (PAHs) are of fundamental importance in the chemistry of circumstellar envelopes of carbon stars,[1] hydrocarbon-rich planetary atmospheres,[2] comet P/Halley, and combustion flames. Despite the crucial role of PAH-like molecules in these environments as a potential precursor to interstellar, carbon-rich grain materials and terrestrial soot particles, well-defined mechanisms verified by a laboratory experiment in the gas phase have not been elucidated. All chemical reaction networks modeling the PAH formation agree that PAH synthesis proceeds via benzene, C$_6$H$_6$.[3] However, the formation of higher molecular weighted (poly)cyclic aromatic hydrocarbon derivatives is still unresolved. Previous studies were restricted to bulk experiments, e.g., the reaction of suprathermal $^{11}$C recoil atoms with liquid benzene at 293 K[4] and arc-generated carbon atoms with solid benzene at 77 K.[5] Since these investigations were performed under bulk conditions, no information on the nascent product distribution is available. In addition, neither the electronic state of the reacting carbon atom nor the kinetic energy is known, and mechanistical conclusions are therefore very speculative.

In this Communication, we present the first crossed molecular beam results on the reaction of C($^3P_j$) with C$_6$D$_6$ under single collision conditions and a well-defined collision energy, combined with high level electronic structure calculations. In these investigations we provide collision energy-dependent doubly differential cross sections to C$_7$D$_6$/C$_7$D$_5$ isomer formation and give valuable clues to the potential importance of such processes in extraterrestrial environments as well as combustion flames.

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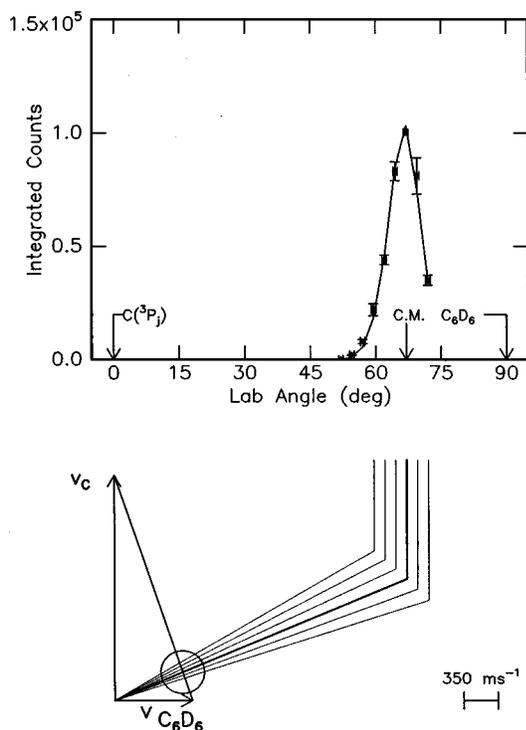g)Electronic mail: hfsiii@arches.uga.edu
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FIG. 1. Lower: Newton diagram for the reaction $C(^3P_j) + C_6D_6$. The circle stands for the maximum center-of-mass recoil velocity in the center-of-mass reference frame of the per-deutero-1,2-didehydrocycloheptatrienyl radical, $C_7D_5$. Upper: Laboratory angular distribution of $C_7D_5$ at $m/e = 94$. Circles and $1\sigma$ error bars indicate experimental data; the solid line indicates the calculated distribution. C. M. designates the center-of-mass angle of 66.4 ±0.8°.
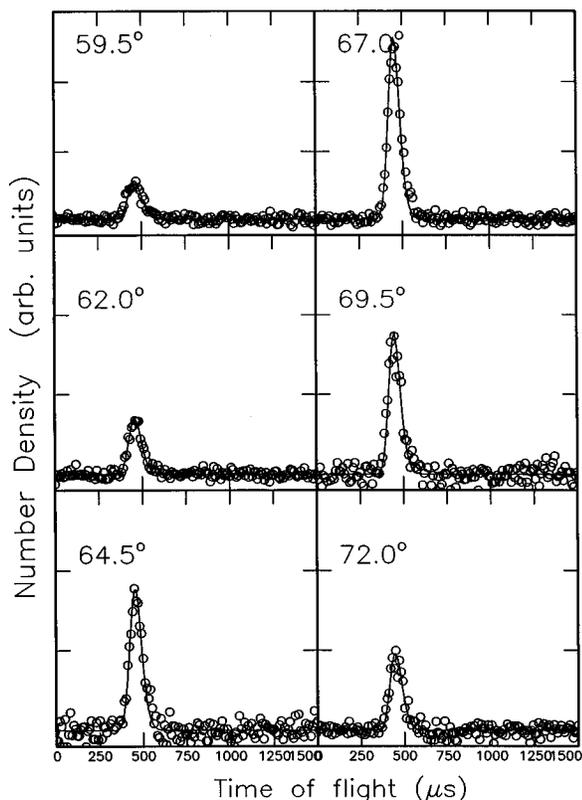


FIG. 2. Time-of-flight data of distinct laboratory angles. The dots indicate the experimental data, the solid lines the calculated fit.



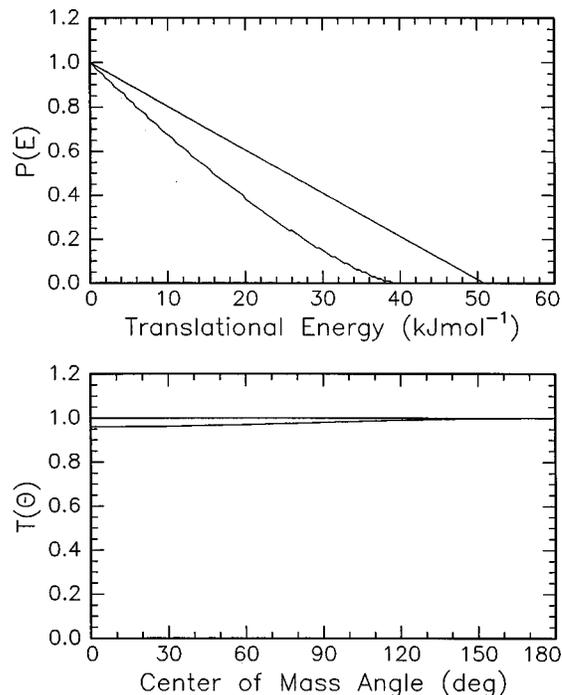FIG. 3. Center-of-mass angular flux (lower) and center-of-mass translational energy flux distributions (upper) for the reaction $C(^3P_j) + C_6D_6$. The solid lines represent the best fits within the upper and lower error limits within $1\sigma$ error bars.

## II. EXPERIMENTAL AND THEORETICAL DETAILS

The experiments are performed with the 35″ crossed molecular beams machine equipped with a triply differentially pumped universal, electron-impact ionizer detector. The detector is rotatable within the scattering plane of the primary and secondary beams from −25.0° to 72.0°. Compared to the original design, as described basically in Ref. 6, the machine was upgraded with magnetically suspended turbomolecular pumps in both the source and main chamber, as well as an oil-free backing pump to ensure oil-free operation. In addition, molecules desorbing from wall surfaces lying on a straight line to the electron impact ionizer were minimized by interfacing a copper plate cooled to 4.5 K and a two stage closed cycle helium refrigerator. During the experiment, a pulsed supersonic carbon atom beam is generated via laser ablation of graphite in the primary source chamber.[7] A four slot chopper wheel located between the skimmer of the primary source and the copper shield, slices a 9 $\mu$s segment of the pulsed carbon beam to select a velocity $v_0 = 2350 \pm 63 \, \text{ms}^{-1}$ and a speed ratio $S = 8.1 \pm 0.3$. The carbon beam crosses a second pulsed beam of 10% benzene seeded in neon carrier gas ($v_0 = 770 \pm 10 \, \text{ms}^{-1}$; $S = 12.7 \pm 0.3$). Time-of-flight spectra of reactively scattered species were monitored using a triply differentially pumped quadrupole mass spectrometer with an electron-impact ionizer in 2.5° steps. To gain information on the reaction dynamics, the time-of-flight (TOF) spectra and the laboratory angular distribution (LAB) are fit using a forward-convolution technique,[8] yielding the translational energy flux distribution $P(E_T)$ and angular distribution $T(\theta)$ in the center-of-mass reference frame.

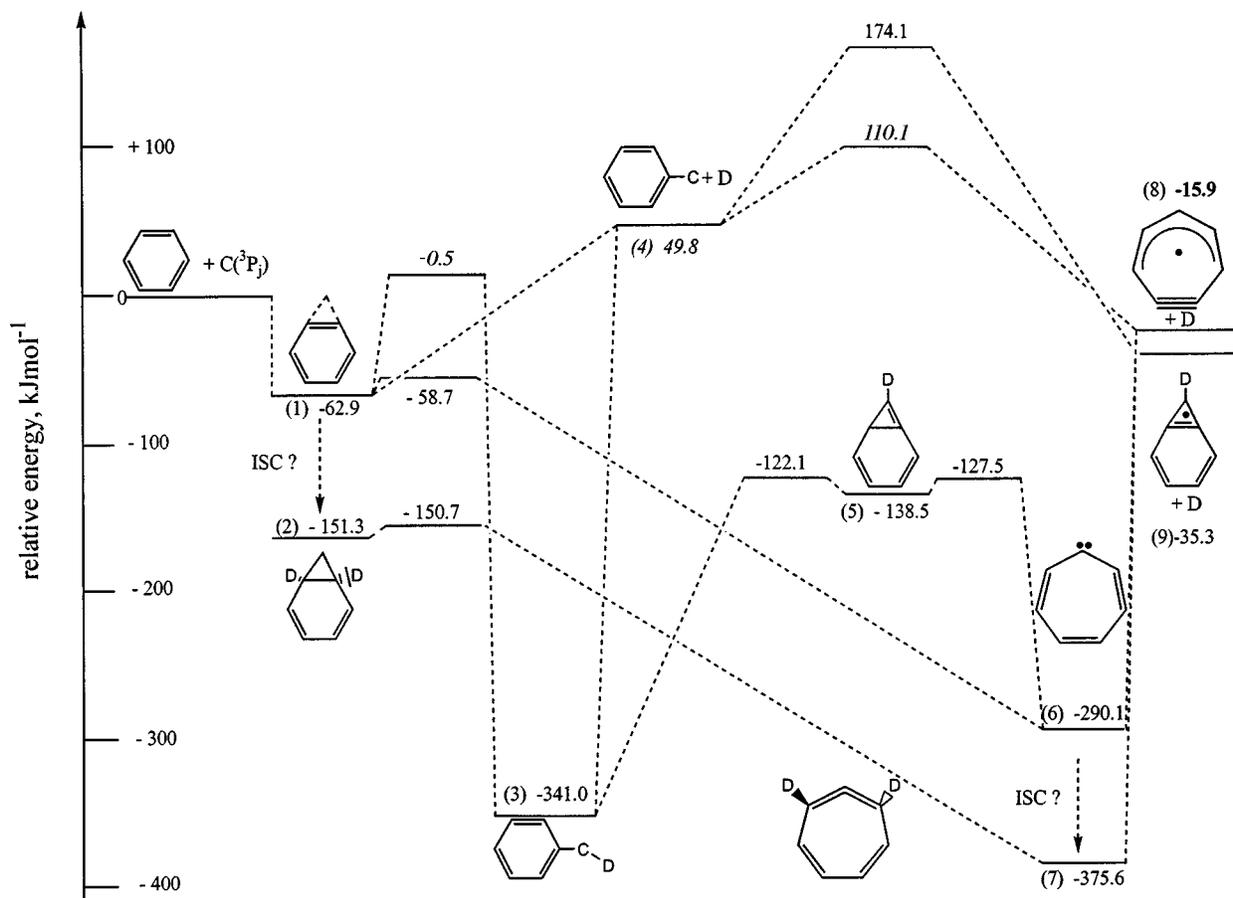The geometries of stationary points of the reactants,

FIG. 4. The schematic energy level diagram for the $C(^3P_j) + C_6D_6$ reaction obtained at the B3LYP/6-311+G**, G2(B3LYP,MP2) (in italics), and CBS-Q (in boldface) levels of theory.

$C_7D_6$ intermediates, and $C_7D_5$ product isomers were optimized with the 6-31G* and 6-311+G* basis set[9] and Becke's[10] three-parameter hybrid functional, in conjunction with the correlation functional of Lee, Yang, and Parr (B3LYP),[11] as implemented[12] in GAUSSIAN94.[13] The spin-unrestricted formalism was employed for all open-shell species; spin contamination was negligible. Harmonic vibrational frequencies and zero-point vibrational energy (ZPVE) corrections were computed at B3LYP/6-31G*. Single-point energies were also computed for selected structures at the G2(B3LYP/MP2)[14] and CBS-Q levels.[15]

## III. RESULTS

A reactive scattering signal was observed at $m/e=94$, i.e., $C_7D_5$, cf Figs. 1 and 2. No $C_7D_6$ adduct could be detected at our collision energy of 32.1 kJ mol$^{-1}$. The LAB distribution of the $C_7D_5$ product (Fig. 1) peaks at 66.5°, i.e., at the center-of-mass angle of 66.4±0.8° within the error limits. The reactive scattering signal is spread over only about 30° in the scattering plane, strongly suggesting that the translational energy released into the $C_7D_5$ product is relatively small. Best fits of our data yield translational energy distributions $P(E_T)$ extending to 38–51 kJ mol$^{-1}$. Taking the relative collision energy into account, the title reaction is exothermic by only 5.9–18.9 kJ mol$^{-1}$. The $P(E_T)$'s shown in Fig. 3 depict a maximum at 0 kJ mol$^{-1}$, implying an exit barrierless fragmentation of the decomposing $C_7D_6$ complex

to the products. The center-of-mass angular flux distribution $T(\theta)$ is isotropic. Within the error limits, a slightly backward peaking of $I(180°)/I(0°)=1.04$ fits the experimental data as well. However, the isotropic distribution gives a better fit. This data suggest that the reaction proceeds either through a long-lived $C_7D_6$ intermediate with a lifetime longer than its rotational period or through a $C_7D_6$ intermediate rotating around a $C_2$ axis. The latter would result in a symmetric exit transition state.[16] In this case, the D atom emission occurs with equal probability to $\theta$ and $\pi-\theta$ and results in an angular distribution symmetric around $\pi/2$. The weak $T(\theta)$ polarization is the result of the weak coupling between the initial **L** and final orbital angular momentum **L**$'$; this suggests that most of the total angular momentum channels into rotational excitation of the $C_7D_5$ product.

## IV. DISCUSSION AND IMPLICATIONS

Our computations show that $C(^3P_j)$ attacks the $\pi$-electron density of the benzene molecule to give (1); cf. Fig. 4. The resulting triplet complex (1) is stabilized by 62.9 kJ mol$^{-1}$ with respect to the reactants and can undergo either intersystem crossing (ISC) to singlet $d_6$-bicyclo[4.1.0]hepta-2,4-diene-7-ylidene,(2), ring opening to $d_6$-cyclohepta-2,4,6-trienylidene,(6), H atom rearrangement accompanied by ring opening to phenylcarbene,(3), or C–D bond cleavage to (4) and atomic deuterium. Singlet (2) can ring open to form singlet (7), which decomposes via

C–D rupture barrierless to the per-deutero-1,2-didehydrocycloheptatrienyl radical, $C_7D_5$, and a D atom. The fate of (6) is governed either by ISC to the singlet surface to (7) or by a decomposition to the per-deutero-1,2-didehydrocycloheptatrienyl radical, $C_7D_5$, and atomic deuterium. Finally, (3) could undergo ring closure to form (5) prior to ring opening to yield (6).

In the following section, we try to narrow these reaction pathways combining our experimental data and the electronic structure calculations. First, we can exclude the involvement of intermediate (4) and the formation of the most stable $C_7D_5$ isomer (9). The reaction to (4) is endothermic by 49.8 $kJ\,mol^{-1}$. This is not achieved since the averaged translational energy of the reactants is 32.1 $kJ\,mol^{-1}$. As the only reaction pathway to the thermodynamically most favorable $C_7D_5$ isomer (9) involves a consecutive insertion into a C–D bond of (4), (9) can clearly be eliminated as the reaction product of the crossed-beams reaction. This is in accord with the high-energy cutoff of our $P(E_T)$: within the error limits, the reaction is exothermic by 5.9–18.9 $kJ\,mol^{-1}$. The formation of the $C_7D_5$ isomer (9), however, corresponds to a calculated reaction exothermicity of 35.3 $kJ\,mol^{-1}$, clearly out of our experiment range. In contrast, the *ab initio* CBS-Q calculations yield 15.9 $kJ\,mol^{-1}$ for the formation of (8), in our good agreement with our experimental data.

Second, intermediate (3) can very likely be ruled out as well since the barrier of (1) to (3) is much higher than the barrier connecting (1) and (6) via ring opening.

Third, the $P(E_T)$'s peaking at zero translational energy indicate that the reaction has no exit barrier. This result is in general agreement with our electronic structure calculations, showing that the endothermic decomposition of either (6) or (7) to form the $C_7D_5$ isomer (8) and atomic deuterium does not require extra energy. Moreover, the C–D bond cleavage must take place at a carbon atom adjacent to the inserted carbon atom to give the carbon–carbon triple bond. However, we cannot elucidate the possible involvement of ISC of (1) or (2) or of (6) to (7). Nevertheless, the intermediates (6) and (7) are bound by a deep potential well, and should have lifetimes longer than their rotational periods. This would give a forward–backward symmetric center-of-mass angular distribution. Future investigations of this reaction and the isotopic counterpart $C(^3P_j)+C_6H_6$ combined with variational RRKM calculations and ISC rate constants will address this problem. Likewise, we will seek to clarify the role of the $C_7D_6/C_7H_6$ adduct formation, which could not be detected by the present experiments. Finally, increasing the collision energy above the reaction endothermicity of 49.8 $kJ\,mol^{-1}$ to form (4)+H might open an additional reaction channel.

Despite these open questions, our investigations showed that there is no entrance barrier for the reaction of atomic carbon with benzene to give an initial complex (1). This finding is of fundamental importance for the chemistry of even the coldest, dark molecular clouds with averaged translational temperatures of about 10 K. Here, benzene molecules can be destroyed upon reaction with atomic carbon to form $C_7H_5$ (8). In contrast, benzene is resistant toward an attack of atomic oxygen at 10 K, where bulk experiments at room temperature indicate an activation barrier between 16.6 and 20.5 $kJ\,mol^{-1}$. Further, $C_7H_5$ could be an important tracer of benzene molecules: unlike $C_6H_6$, our *ab initio* calculation show that this $C_7H_5$ radical has a dipole moment of 1.7 D, which makes it accessible to radio astronomical observation. Likewise, the title reaction could be an alternative pathway to the stepwise reaction of $C_2H_2$ molecules with $C_6H_6$ molecules to form higher, polycyclic aromatic systems and to soot particles in combustion flames.

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