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UV Irradiation of Benzene in N₂ Matrix: A Relevant Study For Titan's Chemistry

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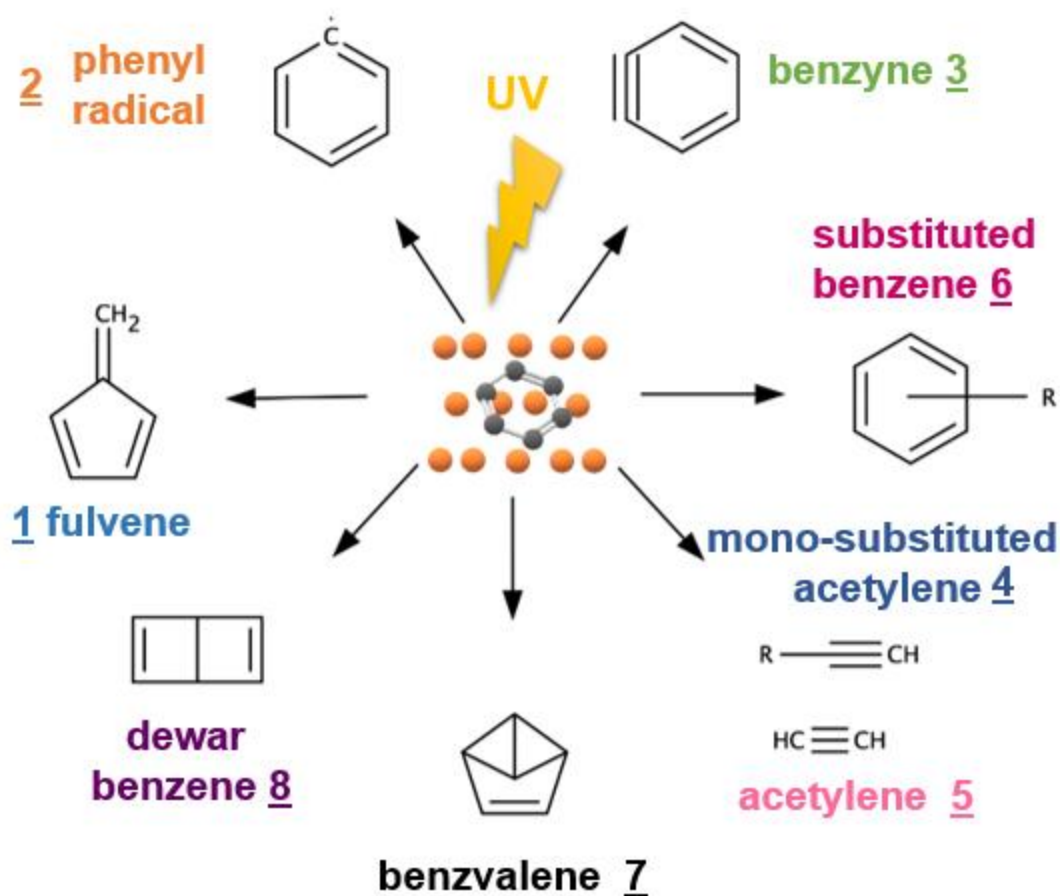
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Highlights:

- Photochemistry at $\lambda > 230$ nm of benzene in solid nitrogen were investigated by infrared spectroscopy
- Fulvene, Dewar benzene, benzvalene, phenyl and benzyne radicals are observed as the photoproducts of benzene by $\lambda > 230$ nm irradiation
- Acetylene derivatives and substituted benzene are also observed after N₂ matrix

Abstract: We report in this contribution the first photochemical study of benzene trapped in solid nitrogen at low temperature (16 K) and irradiated with a mercury lamp ($\lambda > 230$ nm). We identify three benzene isomers (fulvene, Dewar benzene and benzvalene) and two radicals (phenyl and benzyne) as photo-dissociation products, along with acetylene derivatives and substituted benzene. We present for the first time the infrared spectrum of fulvene trapped in benzene ice, which is obtained after nitrogen sublimation. This solid-state characterization could be particularly useful for a better understanding of the photochemical fate of benzene ices recently detected in Titan's atmosphere.

Graphical abstract :



Key words: Titan, Benzene isomers, Fulvene

Introduction

Titan, one of Saturn's moons, is the only body in the solar system having a thick atmosphere, mainly composed of molecular nitrogen and a small percentage of methane[1,2,3]. A variety of organic chemicals (hydrocarbons and nitriles) are formed after photochemical dissociation of these molecules by solar UV photons or high energy particles, and the subsequent recombination of the resulting fragments[4, 5]. Among the different photochemical products, benzene has been discovered in Titan's upper atmosphere. The Ion Neutral Mass Spectrometer (INMS) and Cassini Plasma Spectrometer (CAPS) measured a benzene density profile with mixing ratios ranging from 10^{-7} in the thermosphere[6] to 10^{-10} in the stratosphere[7] (Cassini Huygens mission). This

decrease is considered as an indication of a high altitude source and a low altitude sink of this molecule due to photolysis[8].

Moreover, it is suspected that benzene molecules are at the origin of the organic haze layer[5] that masks Titan's surface by initiating the formation of larger polycyclic aromatic hydrocarbons (PAHs) or polycyclic aromatic nitrogen heterocycles (PANHs)[1,9]. The detection of large amount of benzene vapors[10] as well as several icy benzene-containing massive clouds[11, 12] at altitudes crossed by softer UV solar radiation has been reported. The fate of benzene in Titan's stratosphere before and after its condensation around 85 km is still unknown. To our knowledge, the role of benzene photolysis in the stratospheric production of aerosol particles has not yet been investigated experimentally. However, several experimental studies have identified its role in the composition of highest atmospheric layers. At benzene condensation altitude, only solar photons with $\lambda > 230$ nm[13,14,15] can participate in the photochemistry, the shorter ones being stopped at higher altitude (with a photon flux $\sim 10^7$ photons.cm⁻².nm⁻¹.s⁻¹ over an altitude range corresponding to the benzene condensation[13]). Based on the UV absorption spectrum of benzene published by Dawes et al.[16] (2017), the study of the photochemistry at $\lambda > 230$ nm is completely justified. Indeed, benzene possesses a vibronic structure associated with the $^1B_{2u} \leftarrow ^1A_{1g}$ transition around 255 nm, even if its cross section is 15 times less than the one located around 180 nm ($^1E_{1u} \leftarrow ^1A_{1g}$) and 6 times less than the corresponding to the $^1B_{1u} \leftarrow ^1A_{1g}$ band.

Benzene photo-reactivity can be experimentally reproduced with the help of matrix isolation studies in which benzene is trapped at low temperature in a rare gas matrix. In this environment, benzene molecules are isolated, which can simplify its photochemistry compared to a solid benzene ice. The benzene photochemical behavior in various matrices[17, 18, 19, 20, 21, 22] (Ar, Xe, parahydrogen, halogens, CO, CO₂, H₂O, CCl₄) and submitted to different sources of energy (UV at 193 nm[19, 21] or 253 nm[17, 21], Corona discharge[18] or X-rays[22]) has been largely investigated. These experiments have demonstrated that benzene photochemistry is wavelength and environment dependent [17], resulting in different isomer production rates. However, argon matrices studies are the most numerous in the literature. Moreover, the photolysis performed at 253.7 nm of benzene trapped in argon matrices [17] and in parahydrogen [21], leads to the formation of three isomers: fulvene, benzvalene and Dewar benzene. Thus, experiments performed at low energy in N₂ matrix have two goals. First, to evaluate the influence of N₂ on benzene

photolysis. Indeed, benzene absorption extends to the origin of its first singlet excited state S_1 at 263 nm[23]. Deactivation of the excited electronic states leads to a transient highly excited state ($C_6H_6^*$) which can be quenched by collisions with N_2 [24]. Second, to provide data concerning the products formed during the matrix irradiation, and especially solid fulvene, to examine if they are stable when produced at low energy photons.

A third and more important reason to perform experiments in N_2 matrix is that from all the aforementioned cryogenic studies, none of them resembles Titan's atmospheric conditions. Therefore, as N_2 is the major component in Titan's atmosphere, nitrogen cryogenic matrices are powerful tools for simulating the photochemical activity of molecules present in Titan's atmosphere that can subsequently condense to form ices at lower altitudes, photo-processed, for which few solid-state experimental data are available. Eventually, matrix sublimation leads to benzene amorphous ice in which photoproducts are trapped and can be characterized in solid-state. Their solid-state characterization is particularly important since the recent detection of icy benzene in the lower part of Titan's atmosphere. For all these reasons we decided to conduct a laboratory experiment to understand which products coming from the photochemistry of benzene can condense and contribute to the molecular diversity of the organic surface layer after the sedimentation process. Hence, these data are particularly interesting for the future Dragonfly mission.

In this study, we investigate the photolysis of benzene at $\lambda > 230$ nm using solid nitrogen matrix to characterize the different photoproducts likely to be formed in Titan's stratosphere before benzene condensation, by comparison with previous experiments. We sublime the nitrogen matrix in order to characterize the solid infrared spectrum of fulvene trapped in solid benzene, one of the photoproducts of benzene. In general, we would like to know if the photoproducts obtained during the photolysis in matrix could be formed during the direct photochemistry of the benzene ice that we will perform in a future work.

1. Experimental Details

Benzene (for HPLC, assay $\geq 99.9\%$, from Sigma-Aldrich) is purified by freeze-thaw cycles with the help of nitrogen baths. It is deposited from a glass-line on a copper surface, which temperature

was controlled between 14K to 300K with a closed-cycle helium refrigerator and maintained using a model 21 CTI cold head cryostat, a resistive heater and a Lakeshore 331 temperature controller, within a high vacuum chamber (10^{-8} mbar). The IR spectra are recorded in reflection-absorption mode in the mid-infrared region between 4000 and 600 cm^{-1} using a Fourier transform infrared spectrometer with DTGS detector[25]. Each spectrum is averaged over 100 scans during the experiments, with a resolution of 0.5 cm^{-1} (matrix) or 1 cm^{-1} (solid), except for the background averaged over 300 scans with the same resolutions.

Photolysis experiments are performed using an Oriel 500W high-pressure mercury lamp ($\lambda=200\text{-}2500$ nm) with discrete Hg lines in the UV-Vis region between 200 and 600 nm, and very low irradiance at energies lower than 230 nm.

The gas mixtures (N_2 /benzene (500/1)) used for the matrix isolation experiments are prepared by standard manometric techniques. These mixtures are sprayed onto a copper plate cooled down to 14 K. The sample is warmed using a heated resistance at a temperature below the N_2 desorption temperature (around 40K under our experimental conditions) in order to make the matrix more flexible and then at a higher temperature in order to sublime the nitrogen.

All the experiments described below are done in three steps: (i) photochemical products formation from $\lambda>230$ nm photolysis of benzene; (ii) N_2 matrix annealing; (iii) N_2 desorption at 40K.

For the solid experiment pure benzene was deposited at 16K and then warmed up to 40K with a heating rate of 0.5 $\text{K}\cdot\text{min}^{-1}$. At this temperature the benzene ice is known to be in an amorphous phase[26].

2. Results

2.1. Infrared spectroscopy of benzene in nitrogen matrix at 14K

Figure 1 displays the infrared spectrum of benzene trapped in N_2 matrix (1/500). All the values relative to the infrared absorption bands (wavenumbers and intensities) are listed in Table 1 and are compared to the work of Fredin and Nelandar[27] which is the most detailed published analysis.

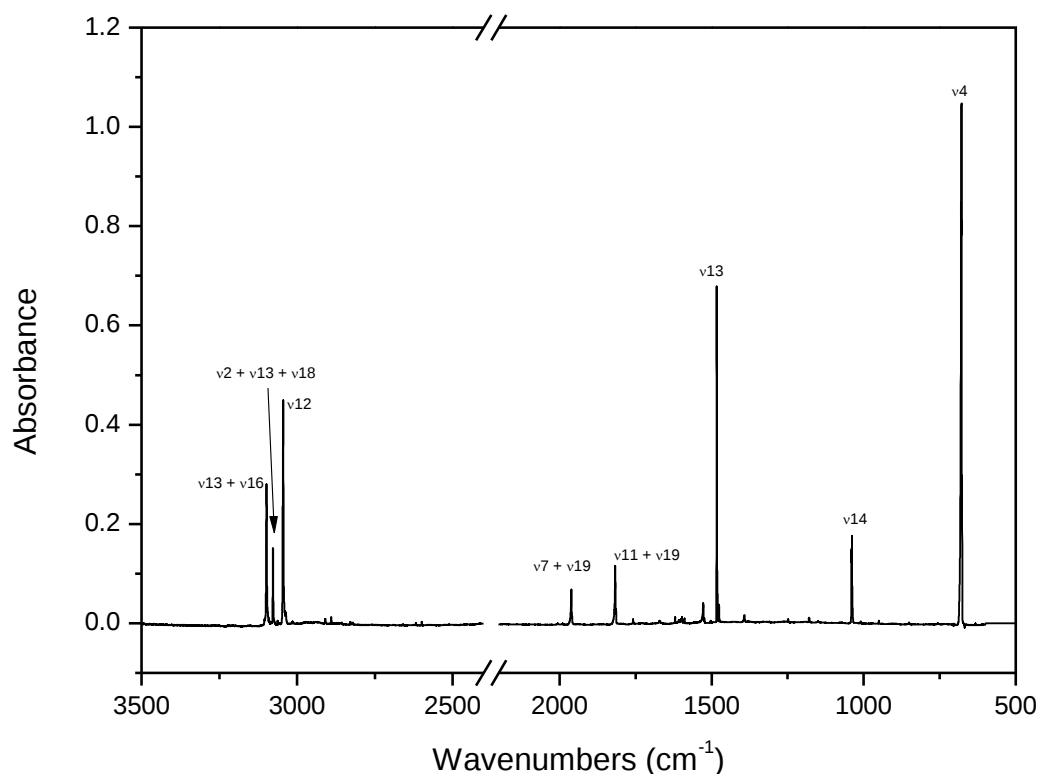


Figure 1: Infrared spectrum of benzene trapped in nitrogen matrix at 14 K. The spectrum has been truncated in the middle in order to omit the gaseous CO₂

The most intense infrared absorption bands of benzene in a N₂ matrix are located at 678.5 cm⁻¹ and 1483.1 cm⁻¹ assigned respectively to γ_{CH} out-of-plane bending mode (ν_4) and $\nu_{\text{C}=\text{C}}$ stretching mode (ν_{13}). The ν_{CH} stretching mode (ν_{12}), typical of aromatic molecules, is located at 3044.4 cm⁻¹. Less intense than the other fundamental modes, the δ_{CH} in-plane bending mode is found at 1038.8 cm⁻¹. Several intense combination modes are located in two different spectral regions. The first region is located in the CH stretching mode area with two bands at 3098.0 and 3077.3 cm⁻¹, respectively assigned to $\nu_2 + \nu_{13} + \nu_{18}$ and $\nu_{13} + \nu_{16}$. The other group includes the $\nu_7 + \nu_{19}$ mode at 1961.1 cm⁻¹ and the $\nu_{11} + \nu_{19}$ mode at 1816.9 cm⁻¹. A complete identification of benzene fundamental and combination modes of this work, along their respective wavenumbers and assignments are listed in Table 1 and compared to earlier published values [27].

Table 1: Experimental vibrational wavenumbers (cm⁻¹) of benzene in solid nitrogen at 14 K and in solid phase at 40 K compared with the study of Fredin and Nelander [27] in nitrogen matrix and in gas phase.

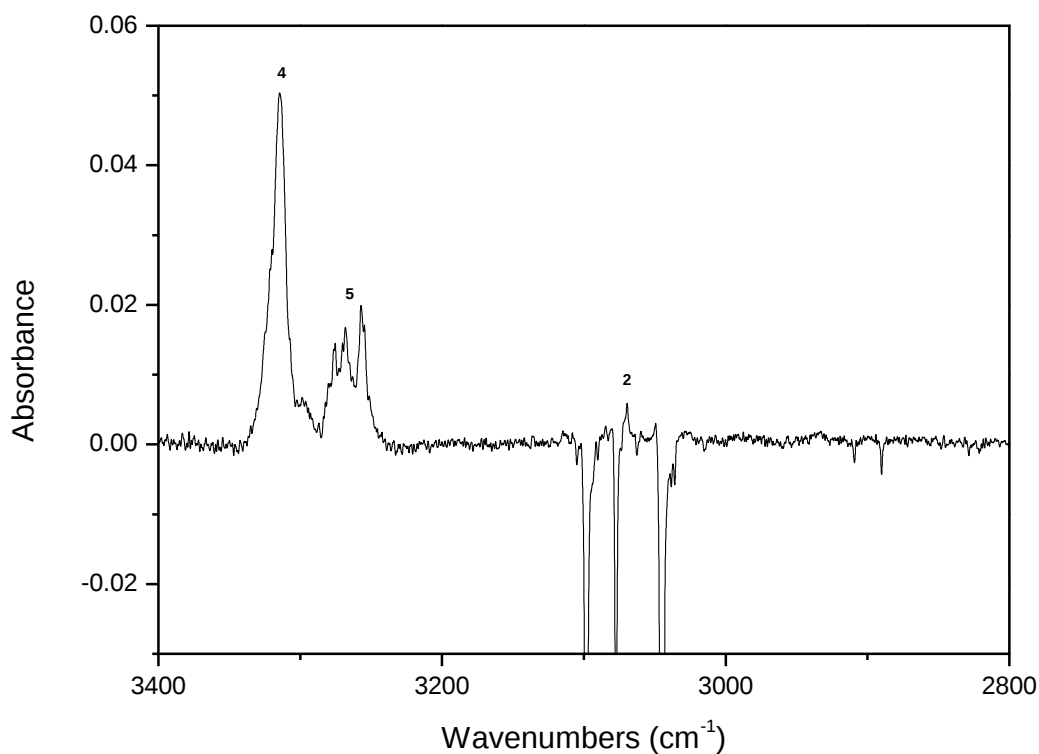
Int: Relative intensities of band:

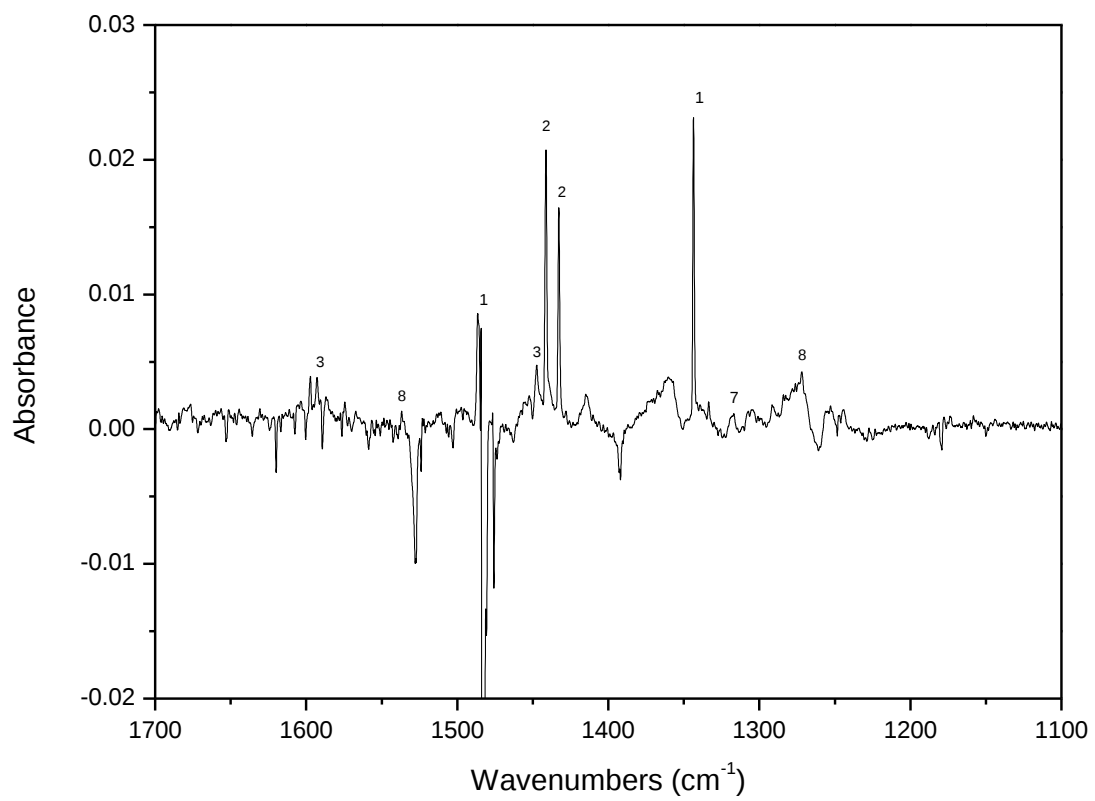
<i>Assignment</i>	<i>Benzene in N₂ matrix (this work)</i>		<i>Benzene in N₂ matrix[27]</i>	<i>Solid benzene 40K (this work)</i>		<i>Benzene in Gas phase[27]</i>
	Wavenumbers	Int.	Wavenumbers	Wavenumbers	Int.	Wavenumbers
$\nu_{13} + \nu_{16}$	3098.0	0.15	3099	3089	0.182	3100
$\nu_2 + \nu_{13} + \nu_{18}$	3077.3	0.068	3077	3070	0.078	3083
ν_1	3073.2	<0.01				3073
ν_{15}	3057.7	<0.01				3056
ν_{12}	3044.4	0.33	3044	3033	0.41	3047
	3014.0	<0.01		3005	0.029	
$\nu_2 + \nu_{18} + \nu_9$	2909.2	<0.01	2908.4	2907	<0.01	2919
$\nu_9 + \nu_{16}$	2890.1	<0.01	2889.4	2887	0.01	2899
	2856.3	<0.01	2855.1			2853
$\nu_3 + \nu_{13}$	2828.6	<0.01	2828.7			2827
	2820.9	<0.01	2820.5	2819	<0.01	
$\nu_2 + \nu_{18} + \nu_6$	2616.7	<0.01	2617.0	2613	<0.01	2620
$\nu_6 + \nu_{16}$	2599.2	<0.01	2598.6	2594	<0.01	2600
$\nu_{14} + \nu_{17}$	2217.9	<0.01	2217	2209	<0.01	2214
$\nu_7 + \nu_{19}$	1961.1	0.063	1961.0	1967	0.05	1958
$\nu_{11} + \nu_{19}$	1816.9	0.096	1816.9	1823	0.092	1811
$\nu_{10} + \nu_{18}$	1758.2	<0.01	1757.9	1754	<0.01	1755
$\nu_8 + \nu_6$	1714.0	<0.01	1713.8	1713	<0.01	1716
$\nu_8 + \nu_{19}$	1671.4	<0.01	1671.1	1675	<0.01	1673
$\nu_6 + \nu_{18}$	1619.8	<0.01	1619.8	1617	<0.01	1622
$\nu_2 + \nu_{18}$	1608.0	<0.01	1607.4	1604	<0.01	1610
ν_{16}	1589.1	<0.01	1589.1	1586	<0.01	1590
$\nu_4 + \nu_{11}$	1527.0	0.03	1527.6	1540	0.044	1522
ν_{13}	1483.1	0.25	1482.9	1478	0.513	1482
$\nu_{13}^{13}\text{C}$	1475.8	0.011	1475.3	1471	0.013	
$\nu_7 + \nu_{20}$	1392.5	0.012	1392.6	1400	0.025	1388
ν_3	1346.2	<0.01		1348	<0.01	1350
ν_9	1309.5	<0.01		1311	<0.01	1309
$\nu_{11} + \nu_{20}$	1248.4	<0.01	1248.2	1242	<0.01	1242
ν_{17}	1179.0	<0.01	1180.0	1176	0.06	1178
ν_{10}	1150.0	<0.01		1146	0.03	1146
ν_{14}	1038.8	0.13	1039.8	1035	0.37	1037

ν_6	1009.2	<0.01	1009.1	1011	0.01	1010
ν_2/ν_7	992.4	<0.01		998	0.02	993
ν_{19}	969.6	<0.01		973	0.02	967
ν_{11}	850.3	<0.01		854	0.04	846
ν_8	698.8	<0.01	698.8	705	0.01	707
ν_4	678.5	1	678.6	674	1	673
ν_{18}	608.0	<0.01		607	<0.01	606

2.2. Irradiation of benzene in nitrogen matrix at 14 K

When matrix isolated benzene is submitted to radiation at $\lambda > 230$ nm, we observe the decrease (30% after 3025 min of irradiation) in its infrared features along with the apparition of new absorption bands in different spectral regions. Figure 2 presents subtraction spectrum between the last irradiation time (3025 min) and the time before photolysis of the deposited matrix. The bands that grow during irradiation appear in positive and those that decrease (benzene ones), in negative.





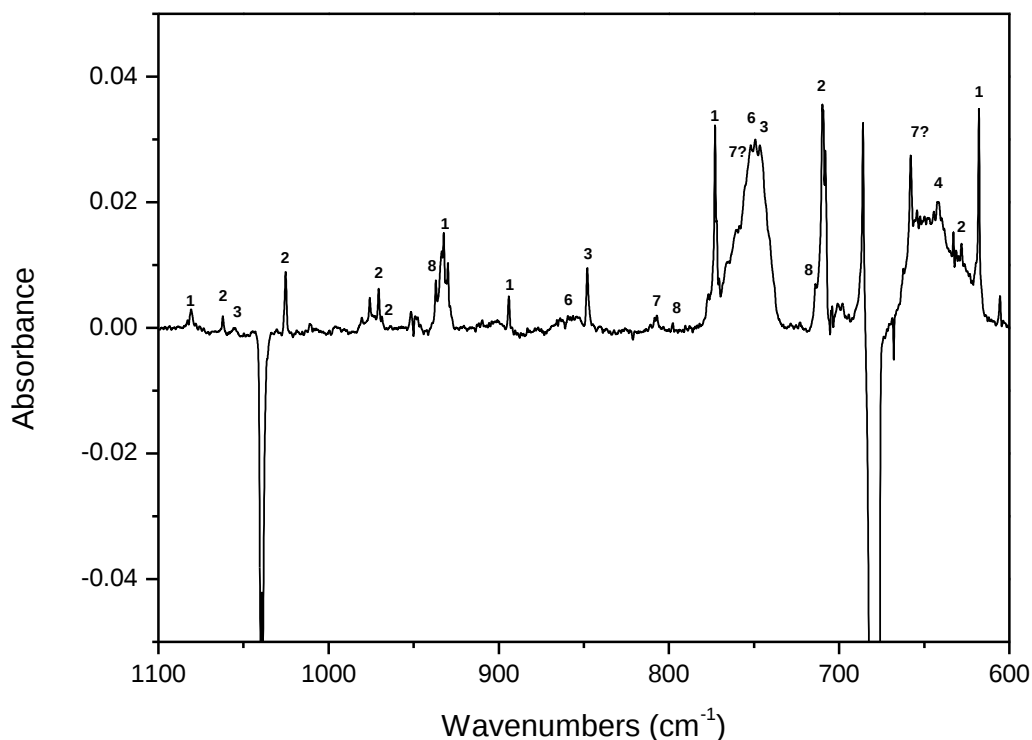


Figure 2: Subtraction spectrum between the last irradiation time (3025min) and before irradiation of benzene in N₂ matrix performed at $\lambda > 230$ nm. Negative bands correspond to the benzene one and positive bands correspond to products formed during the experiment
1: fulvene. 2: phenyl radical. 3: benzyne. 4: substituted acetylene. 5: acetylene. 6: substituted benzene. 7: benzvalene. 8: Dewar benzene.

The absorption bands, produced during the experiment, are listed in Table 2 and 3. Peak attribution is based on previously published data [19, 21, 29, 30, 31, 32] taking into account a reasonable shift due to the nitrogen matrix. Indeed, various rigid host matrix may trap a guest molecule in different local environments where these molecules may undergo slightly different external fields or geometrical constraints. Consequently, the frequencies of certain vibrationnal modes may be shifted, either through the influence of the varying external field on the electronic structure of a host molecule, or through an increase in a force constant when the atoms have to work against the rigid environment along some normal mode. So, depending on the type and size of the host

material, or on charge transfer effect, this can lead to small frequency shift. So, Perchard et al.[28] have shown that the shift could be up to 14 cm^{-1} between argon and nitrogen matrix.

For those bands with sufficient intensity, it is sometimes possible to correlate their evolution as a function of the irradiation time and to sort them into different groups, according to their behavior. This step allows to potentially confirm assignments. In general, dissociation and isomerization pathways are similar between the different matrices except if N_2 quenches the photoreactivity as predicted in gas phase [9].

2.2.1. Fulvene identification

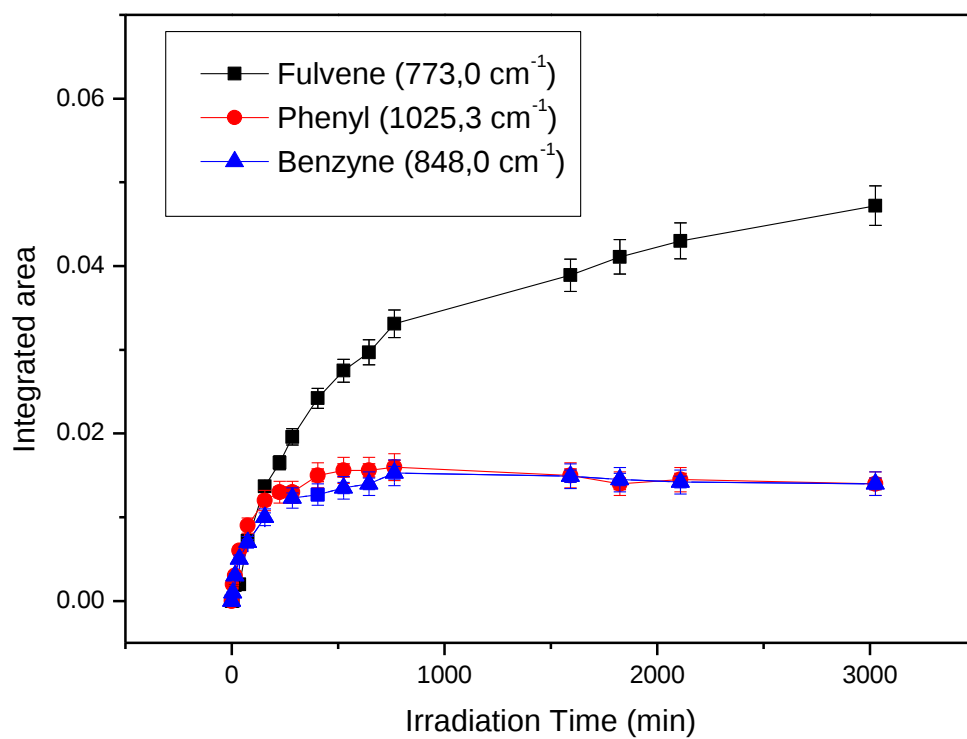
Fulvene **1** is a well-known product of benzene photolysis and has been characterized previously isolated low temperature matrices [19, 21, 29]. Using literature values and results of theoretical calculation (B3LYP/6-311+G(d,p) [21], absorption bands at 1486.4, 1343.6, 1080.7, 932.4, 894.0, 773.0 and 617.8 cm^{-1} are attributed to fulvene. Further confirmation of this assignment comes from the similar evolution of the most intense absorption bands (773 cm^{-1} as a function of 617.8 and 1343.6 cm^{-1} , correlation factor 0.99) pictured in figure S1). All these bands are well known and are in good agreement with those previously reported by Toh et al.[21] in para hydrogen matrix and Griffith et al.[29] or Laboy et al.[19] in argon matrix (Table 2). The evolution of the integrated area as a function of the irradiation time of the absorption band at 773 cm^{-1} assigned to fulvene is reported in Figure 3. It demonstrates that the amount of this isomer continues to increase throughout the duration of the photolysis. Nevertheless, comparison with literature spectra [19, 21] for this isomeric species leads to the conclusion that only the most intense bands are observed in our experimental conditions (Table 2). Indeed, no absorption bands obtained by Laboy et al.[19], Griffith et al.[29] or Toh et al.[21] above 3000 cm^{-1} are observed. This is not surprising since these bands are the smallest in experiments performed both in Argon and parahydrogen matrix.

Table 2: Experimental vibrational wavenumbers of fulvene in solid N_2 compared with those in Ar matrix and solid parahydrogen

Fulvene 1			
Our Work	Laboy et al.[19]	Griffith et al. [29]	Toh et al.[21]

N₂ Matrix (1/500)	<i>Int</i>	Ar Matrix (1/250)	<i>Int</i>	Ar Matrix	<i>Int</i>	pH₂	<i>Int</i>
		3157	0.071			3104.7	0.01
		3116	0.155	3104	w		
				3088	m	3088.0	0.05
				3008	s	3007.6	0.03
		1857	0.097				
		1853	0.233				
1486.4	0.12	1488	0.422	1486	s	1486.1	0.25
		1486	0.352			1485.5	0.12
1343.6	0.59	1342	0.778	1342	s	1342.6	0.46
		1334	0.169				
1080.7	0.07	1080	0.288	1077	m	1078.5	0.09
932.4	0.45	926	1.198	926	s	927.9	0.74
		908	0.166	907	m	907.5	0.06
894.0	0.14	894	0.427	894	m	895.3	0.16
773.0	1	770	1.626	769	s	779.0	1
617.8	0.98	615	1.293	613	vs	616.4	0.58

206 .
207



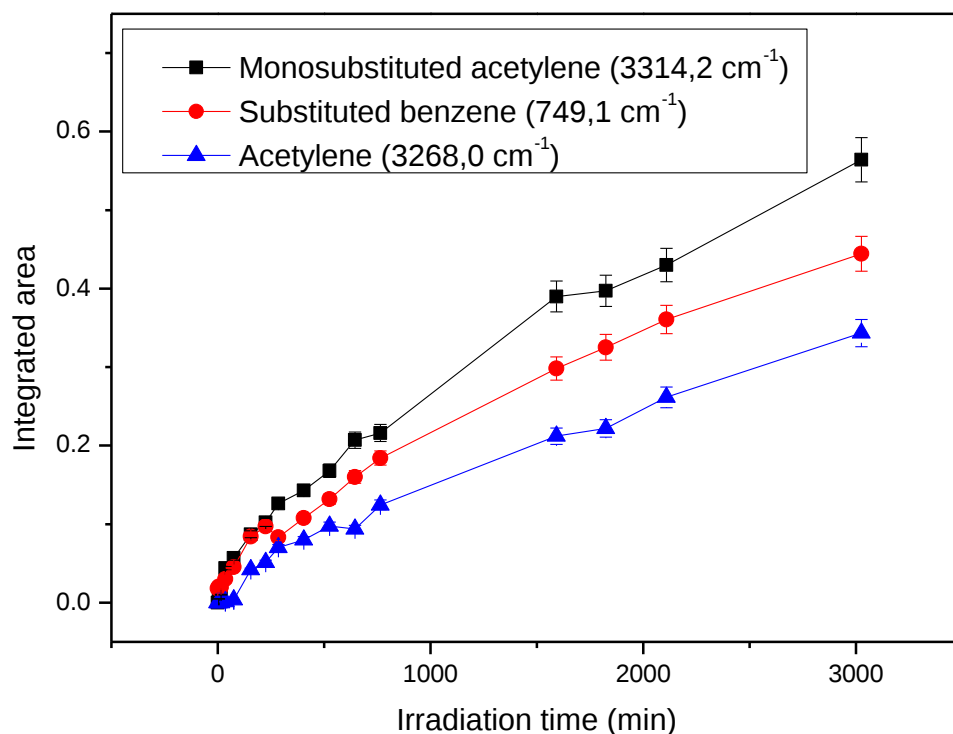


Figure 3: Evolution of the integrated absorbance of fulvene, phenyl radical (top) and monosubstituted acetylene, substituted benzene and acetylene (bottom) with error bars, during the photolysis ($\lambda > 230$ nm) of benzene in nitrogen matrix (1:500). The error bars correspond to the discrepancy of the different integration performed.

2.2.2. Identification of other products

Two groups of absorption bands increase then decrease during irradiation (Figure 3). The first one, composed of absorption bands at 3070.7, 1441.3, 1432.7, 1062.0, 1025.3, 975.6, 970.7, 709.7 and 628.2 cm⁻¹, is assigned to the phenyl radical **2** based on previous works[30,31] (Table 3). The intensity of the 1025.3 cm⁻¹ absorption band plots as a function of the one at 709.7 cm⁻¹, is presented in figure S2 as well as 3070.7 cm⁻¹ as a function of 1025.3 cm⁻¹ and 970.7 cm⁻¹ as a function of 975.6 cm⁻¹ (Supplementary material). The bands at 3070.7 and 970.7 cm⁻¹ are too weak to be plotted as a function of the two others. All of the bands obtained in our study are the same as

227 the most intense formed in an Ar matrix and reported by Radziszewski et al. [31]. Only shifts of
228 about 1 cm⁻¹, coming from the difference between the experimental conditions (N₂ versus Ar), are
229 observed.
230

Benzvalene 7						Dewar Benzene 8					Phenyl 2				Benzyne 3						
Our work		Griffith et al.[28]		Toh et al. [21]		Our work		Griffith et al.[29]		Toh et al.[21]		Our work		Radziszewski et al. [31]		Our work		Dunkin et al.[32]		Radziszewski et al.[31]	
N ₂ Matrix (1/500)	Int	N ₂	Int	pH2	Int	N ₂ Matrix (1/500)	Int	Ar Matrix	pH2	Int	N ₂ Matrix (1/500)	Int	Ar Matrix	Int	N ₂ Matrix (1/500)		N ₂ Matrix		Ar Matrix	Int	
1316.1	0.8	3128	w					3134	w	3133.6	0.06			3085	0.19					3094	0.07
		3092	s							3111.5	0.12	3070.7	0.20	3073	0.19			3088		3086	0.11
		3072	s	3071.6	0.04			3112	m	3110.9	0.15									3071	0.01
				3066.2	0.01					3108.9	0.05									3049	0.01
		1553	m	1554.8	0.13			3107	m	3107.8	0.06							2084			
		1314	s	1313.3	0.2			3069	m	3069.6	0.15									1846	0.02
		1240	m	1239.6	0.02					3058.8	0.07			1499	0.04			1598			
		1183	m	1182.7	0.04			3046	s	3048.8	0.10	1441.3	0.28	1441	0.16	1447.9	0.42	1448		1451	0.11
		1163	ms	1163.8	0.06			2986	vs	2984.7	0.05	1432.7	0.27	1433	0.11					1394	0.07
		1097	w	1090.4	0.09	1536.0	0.16	1539	vs	1535.5	0.10									1271	0.02
807.1	1							1536	vs											1094	0.02
		1090	vs	1089.5	0.28			1284	m	1282.1	0.07			1226	0.06						
								1281	m												
		850	ms	849.1	0.11	1271.9	0.43	1270	s	1268.1	0.16					1054.0	0.16	1056		1055	0.09
								1268	s												
		812	s	811.6	0.24			1149	ms	1146.8	0.04			1080	0.04			1039		1039	0.13
								1147	ms												
		763	mw	760.4	0.03			1135	ms	1134.8	0.11	1062.0	0.07	1067	0.02					982	0.06
		747	vvs	742.8	0.34	937.0	1	938	ms	935.4	0.09	1025.3	0.21	1027	0.14	848.0	1	847		849	0.31
								936	ms												
744.7	?	744	vvs	741.1	1			928	ms	928.8	0.41							740.6	?	743	
657.9	?	651	m	-	-			923	m	923.3	0.08	975.6	0.05	976	0.03			472		472	1
								826	s	822.9	0.22	970.7	0.06								
								823	s												
						793.0	0.15	795	vvs	792.3	1.0										
								793	vvs												
						704.1	0.45	709	s	702.2	0.47	709.7	1	708	1						
								705	s												
												628.2	0.01	629	0.19						

Table 3: Experimental vibrational wavenumbers of Benzvalene **7, Dewar benzene **8**, Phenyl **2** and Benzyne **3** in solid N₂ compared with those in Ar matrix, nitrogen matrix and solid parahydrogen**

The second group composed of four other bands (1447.9, 1054.0, 848.0 and 740.6, cm^{-1}) present the same behavior during irradiation (two panels in figure S3 with 848.0 cm^{-1} plotted as a function of the other features (740.6 and 1447.9 cm^{-1}) and having correlation factors of 0.985 and 0.982). These new bands are assigned to benzyne **3** (Table 3). Our assignment of these peaks are confirmed by comparison with previous experimental works performed in argon matrix[18, 19], nitrogen matrix,[32] and parahydrogen matrix[21]. These bands were assigned to o-benzyne on the basis of the parahydrogen matrix work of Toh et al. [21] in which three bands of o-benzyne were identified at 1057, 844 and 735 cm^{-1} . The appearance of o-benzyne is not surprising since it is the most stable of the three benzyne isomers.

Based on previous works[18, 19, 21, 33], the intense band observed at 3314.2 cm^{-1} and the broad one observed at 652.0 cm^{-1} can be assigned to a $\equiv\text{C-H}$ stretching mode and C-H out of plane bending mode of monosubstituted acetylene **4**. The presence of two other broad bands observed at 854.0 and 749.1 cm^{-1} in matrix will be discussed in the next section.

Finally, three bands, observed at 1316.0, 807.1 and 744.7 cm^{-1} are attributed to benzvalene **7** based on the work of Griffith et al.[29] performed in N_2 matrix (Table 3). As observed by Toh et al. [21], only three bands are strong. They are located at 1313.3 cm^{-1} , 811, 6 cm^{-1} and 742.8 cm^{-1} in their parahydrogen matrix. Other bands observed by Toh et al. [21] have lower intensities and are not observed in our experiments. Based on the work of Griffith et al. [29] the band at 657.9 cm^{-1} might also be attributed to this isomer. However, due to the fact that the band at 657.9 cm^{-1} grows on top of a larger feature in our spectrum and is not among the most intense features in other N_2 matrix experiments [29], this assignment remains tentative.

Based on the work of Johnstone and Sodeau [17], Griffith et al. [29], and Toh et al. [21], the formation of Dewar benzene in our experimental conditions can be considered by the growth of new bands at 1536.0, 1271.9, 937.0, 793.0, and 704.1 cm^{-1} , but these bands are too weak to be correctly integrated in order to plot the evolution of one band in function of the others. Moreover, the band at 937 cm^{-1} is very close to a fulvene band and could be assigned to this fulvene band,

which would be structured because of matrix site. All the other bands obtained in the experiments developed in parahydrogen [21] or argon matrix [29] are lower in intensity than the ones we get (Table 3). Although these five bands are observed in our experiment, their low intensities (preventing their correlation) do not allow us to conclude formally on the formation of this isomer in our experiment.

Since the obtaining of Dewar benzene and benzvalene is not certain in our experimental conditions, we will not discuss them in the rest of this paper.

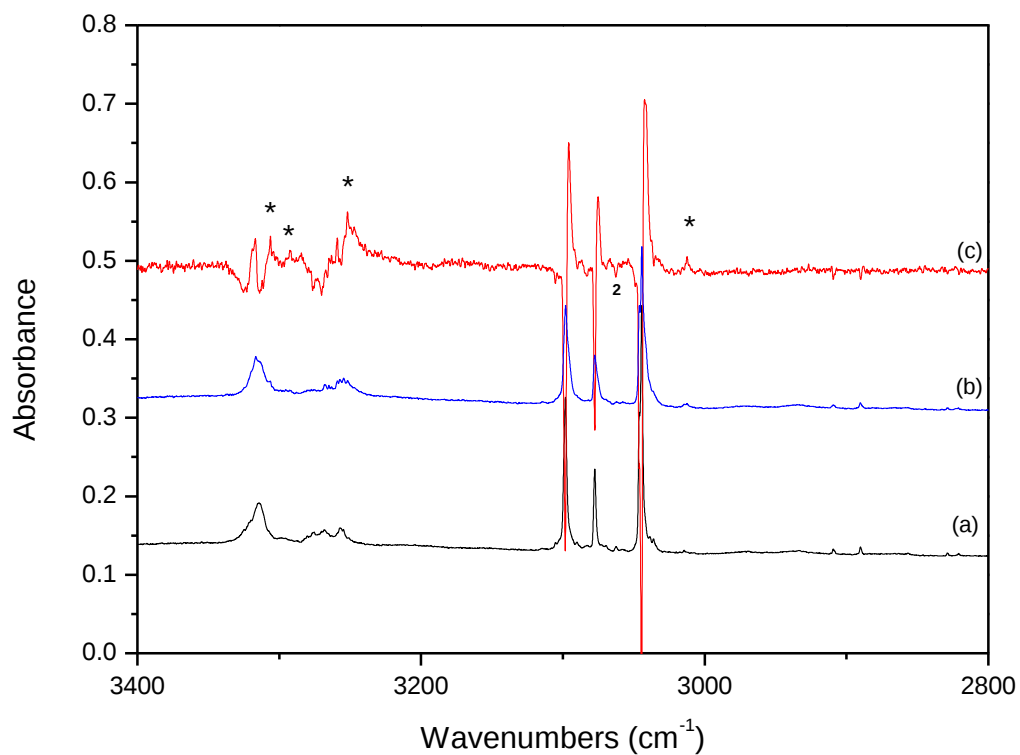
2.3. Matrix annealing

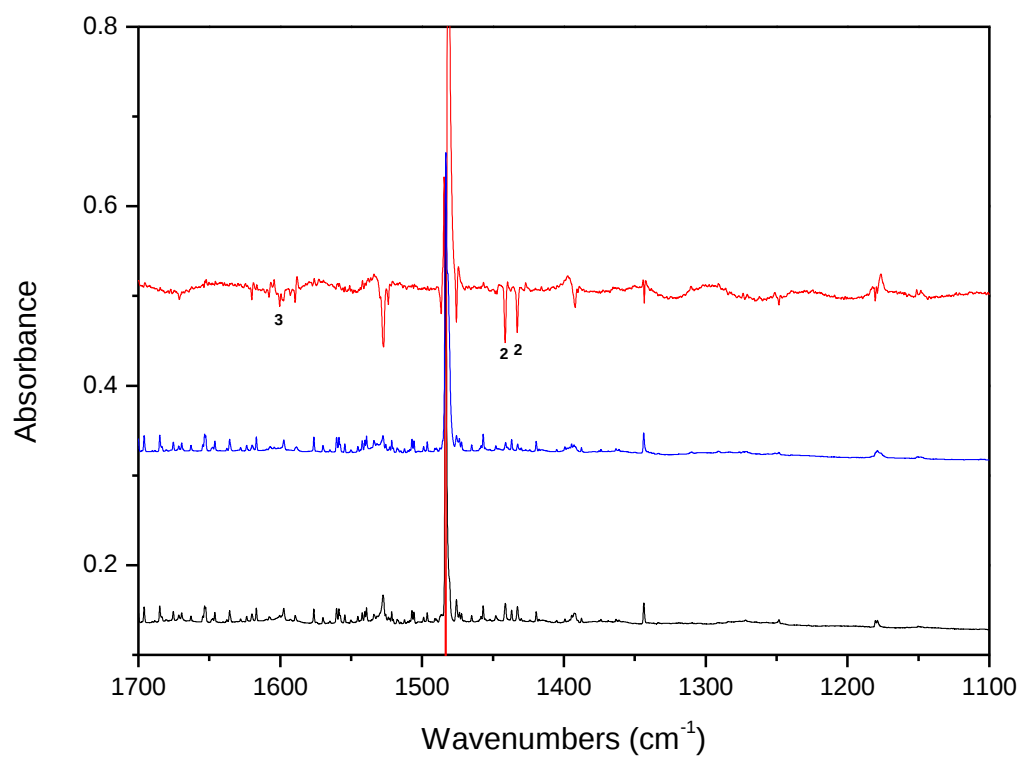
The second step of our experiment is an annealing step, in which the matrix is heated to 30 K for 10 min and then cool down the system back to 14 K. Warming of the sample increases the diffusion coefficient of embedded species without desorbing the matrix host, allowing them to reorient or even migrate through the matrix.

In particular, radicals may be able to exit from their matrix cage during annealing and participate radical-radical recombination or radical-neutral addition elimination process [34,35]. These processes result in changes in the bands which facilitate their assignment. Annealing the irradiated sample result in changes in the difference infrared spectrum (Figure 4). The study is focused on the 3500-2800, 1700-1100 and 1200-600 cm^{-1} regions where most of the new absorption bands are obtained during the photolysis. With the exception of bands attributed to acetylene monomer, negative bands correspond to phenyl or benzyne radicals which are consumed during annealing through recombination or reaction with other species. Only few bands clearly increase during the matrix annealing at 30 K located at 3317, 3306, 3252, 3013, 652, 640 and 625 cm^{-1} (noted with an asterisk on Figure 4). These bands can come from the formation of dimers, trimers, or multimers of acetylene or acetylene derivatives. Indeed, the absorption bands which grow at 3252 and 625 cm^{-1} are attributed to an acetylene tetramer based on literature reports of the annealing of acetylene trapped in argon matrix [36]. Based on the work of Karir and Viswanathan[37], the bands at 3317, 3306, 652 and 640 cm^{-1} could be assigned to phenylacetylene.

Friderichsen et al. [30] have shown that phenyl radicals can recombine in a cryogenic argon matrix during an annealing performed up to 45 K, to form diphenyl. This molecule has two particularly intense absorption bands at 738 and 699 cm^{-1} , based on spectroscopic data from Martin-Drumel et

al.[38] However, none of these bands are observed on the infrared spectrum obtained after our annealing experiment to 30 K. Sufficient mobility of phenyl radicals is probably not obtained to form biphenyl before our matrix sublimed at 45 K.





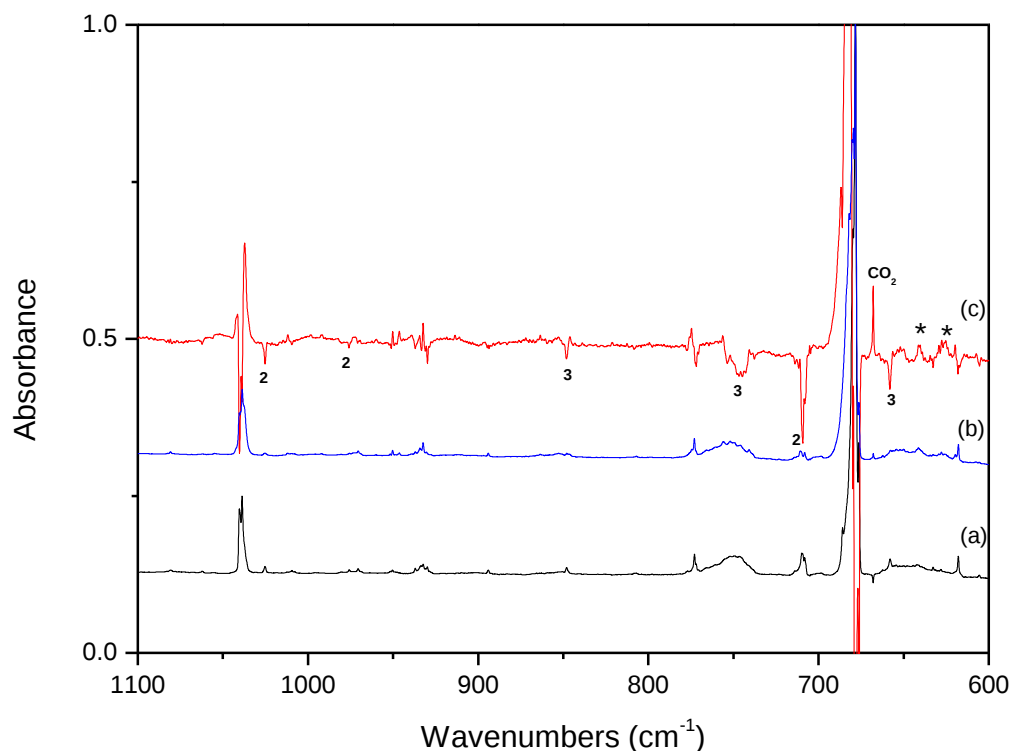


Figure 4: Infrared spectrum of benzene/N₂ after irradiation at 14 K (a) at 14 K after 30 K (b) and subtraction spectrum (c). * correspond to the products formed during the annealing. 2: phenyl radical. 3: benzyne radical

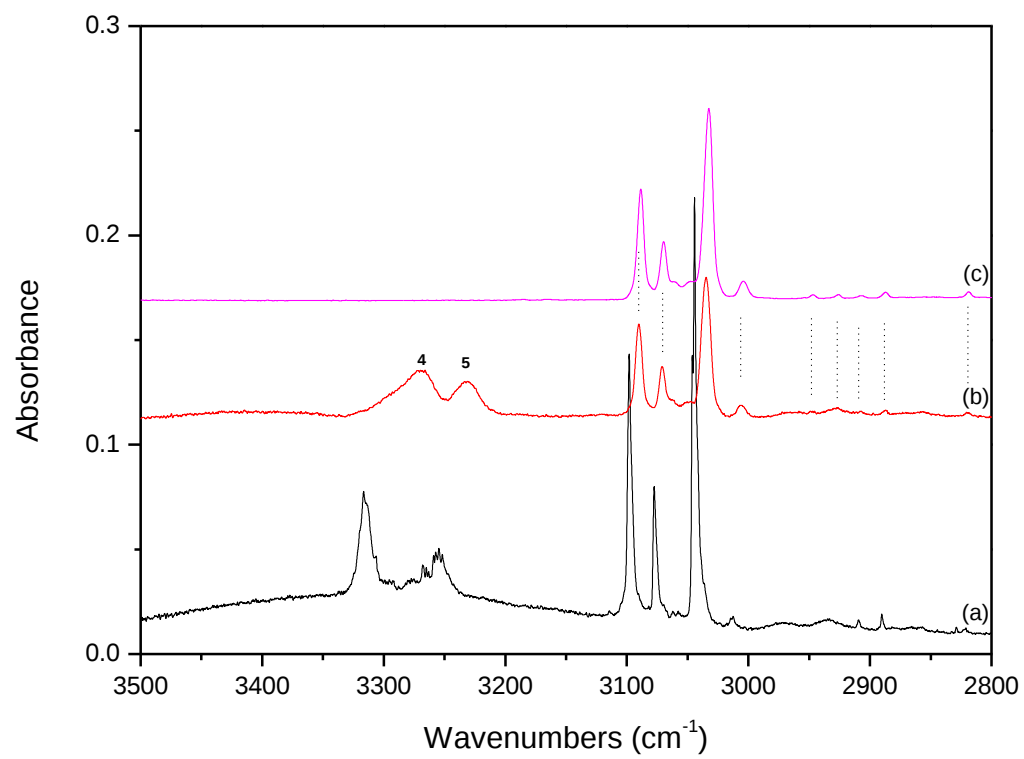
2.4. N₂ sublimation. Identification of solid infrared spectrum of fulvene in benzene

In order to confirm our assignments and investigate the IR spectra of these products that could be obtained in an amorphous state, the solid gas matrix was evaporated by carefully heating the matrix above 30 K. This step allows in particular the identification of the solid infrared spectrum of fulvene trapped in solid benzene. The spectrum obtained at 40 K just after the N₂ sublimation is presented in Figure 5b and compared to the spectrum obtained at 14 K at the end of the irradiation (Figure 5a). Warm-up of the matrix above 40 K induces spectral changes (widening and frequency shift of all the absorption bands as previously observed in matrix-annealed experiments[39, 40, 41] without appearance of any new bands). The infrared spectrum obtained after sublimation (Figure 5a) is dominated by benzene ice signatures. By comparing a spectrum of benzene ice formed by vapor condensation of pure C₆H₆ at 40 K (Figure 5c) with this spectrum,

photoproducts which remain in the solid phase can be seen more easily (Figure 5b) Despite the disappearance of several bands during the warming-up, numerous other bands, previously assigned to different benzene photoproducts (Table 4), are still present in the amorphous ice at 40 K, which makes their solid-state assignment possible.

After sublimation of the N₂ matrix at 40 K, we observe the total loss of bands characteristics of the phenyl and benzyne radicals whereas fulvene bands are only shifted by 2 to 6 cm⁻¹ between the cryogenic matrix and the solid phase. The solid absorption bands remaining at 1339, 1076, 939, 896, 778 and 622 cm⁻¹ are assigned for the first time to this isomer in solid phase surrounded by benzene ice.

From the start of the irradiated matrix heating until after N₂ sublimation temperature (40 K), the features of isolated monosubstituted acetylene (3314.2 cm⁻¹) or acetylene (3275.4, 3268.0 and 3257.0 cm⁻¹) disappear and bands around 3270 cm⁻¹ and 3231 cm⁻¹ increase in intensity because of the sublimation of the matrix. Strazzula and Baratta [33] assigned the increasing bands to solid monosubstituted acetylene and C₂H₂ aggregates. The two intense bands at 753 and 854 cm⁻¹ remain at 40 K and correspond to substituted benzene as previously observed by Strazzula and Baratta [33].



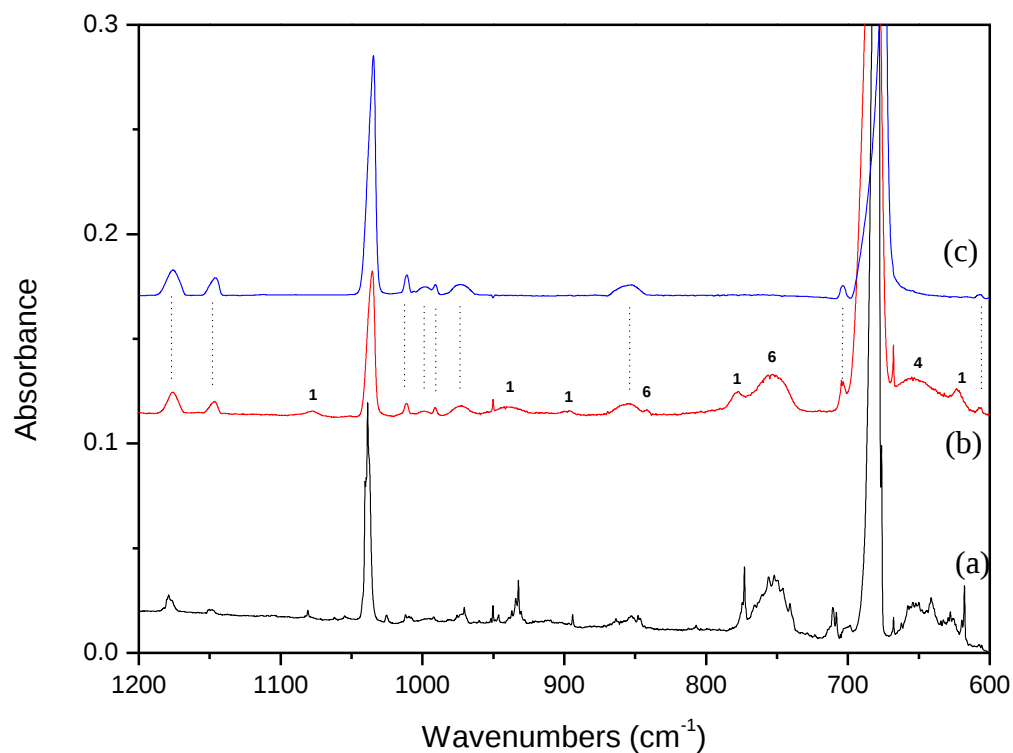


Figure 5: Infrared spectra recorded during the warming-up performed at the end of the photolysis experiment ($\lambda > 230$ nm) of benzene trapped in N_2 matrix: (a) at 14 K after 30K, (b) at 40 K after N_2 sublimation (c) benzene ice at 40K
1:fulvene. 4: substituted acetylene. 5: acetylene. 6: substituted benzene.

Table 4: Experimental wavenumbers (cm⁻¹) of main photoproducts of benzene photolysis performed in Nitrogen matrix and in solid phase (after N₂ sublimation)

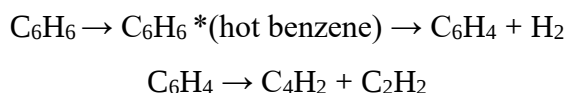
Band (cm ⁻¹)		Assignment	References	
N ₂ matrix	solid			
617.8	622	Fulvene	<u>1</u>	[17]
628.2		Phenyl radical	<u>2</u>	[17, 19, 30, 31]
652.0	652	C-H out-of-plane bending (monosubstituted acetylene/phenylacetylene)	<u>4</u>	[19, 33, 37]
657.9		Benzvalene	7	[29]
704.1		Dewar benzene	<u>8</u>	[21, 29]
709.7		Phenyl radical	<u>2</u>	[17, 19, 30, 31]
740.6		Benzyne	<u>3</u>	[18, 19]
744.7		Benzvalene	<u>7</u>	[21, 29]
749.1	753	C-H out of plane (substituted benzene/phenylacetylene)/ (C ₂ H ₂) ₂ / Benzvalene	<u>6, 7</u>	[19, 33, 37]
773.0	778	Fulvene	<u>1</u>	[17]
793.0		Dewar benzene	<u>8</u>	[21, 29]
807.1		Benzvalene	<u>7</u>	[17, 19, 21, 29]
848.0	841	Benzyne	<u>3</u>	[18, 19, 32]
854.0	854	C-H out of plane (substituted benzene)	<u>6</u>	[33]
894.0	896	Fulvene	<u>1</u>	[17, 18, 19]
932.4	939	Fulvene	<u>1</u>	[17, 18, 19]
937.0		Dewar benzene	<u>8</u>	[17]
970.7		Phenyl radical	<u>2</u>	[30, 31]
975.6		Phenyl radical	<u>2</u>	[30, 31]
1025.3		Phenyl radical	<u>2</u>	[30, 31]
1054.0		Benzyne	<u>3</u>	[18, 19, 32]
1062.3		Phenyl radical	<u>2</u>	[29, 30]
	1077	CH in plane (substituted benzene)	<u>6</u>	[33]
1080.7	1077	Fulvene	<u>1</u>	[17, 18, 19]
1271.9		Dewar benzene	<u>8</u>	[17, 19, 21, 29]
1316.1		Benzvalene	<u>3</u>	[17, 19, 21, 29]
1343.6	1339	Fulvene	<u>1</u>	[17, 18, 19]
1432.7		Phenyl radical	<u>2</u>	[30, 31]
1441.3		Phenyl radical	<u>2</u>	[30, 31]
1486.4		Fulvene	<u>1</u>	[17, 18, 19]
3070.7		Phenyl radical	<u>2</u>	[30, 31]
3257.0		(C ₂ H ₂) ₂		[19]

3268.0	3231	Acetylene/Acetylene aggregates	<u>5</u>	[19, 33]
3275.4		(C ₂ H ₂) ₂		[19]
3314.2	3270	Triacetylene or ≡C-H (monosubstituted Acetylene/phenylacetylene?)	<u>4</u>	[18, 19, 33, 37]

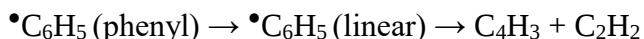
Discussion

We have studied the photolysis of benzene at $\lambda > 230$ nm in N₂ cryogenic matrix in order to try to understand (i) what kind of photo-chemical processes take place in Titan's stratosphere when vapour benzene is submitted to soft energy photons, (ii) if nitrogen plays a role in the photolysis and (iii) if the products formed are stable under these conditions. Our studies show the formation of the benzene isomer fulvene, as well as phenyl and benzyne radicals, monosubstituted acetylene and substituted benzene (Figure 6). Since all the products formed have already been obtained in previous experiments, the nitrogen matrix does not promote formation of new products although it does affect the relative amounts of formed products as already observed in previous experiments [17, 21, 29]. As illustrated in Figure 3, acetylene, monosubstituted acetylene and substituted benzene are formed during all the photolysis experiment in a relative great amount. This result indicates that they are stable when produced by low energy photons in the presence of N₂ and benzene.

As postulated by Yokoyama et al. when benzene is excited to S₁ (which is permit at $\lambda > 230$ nm), H₂ and CH₃ eliminations occur from hot benzene. Some of C₆H₄, produced absorb another photon and dissociate to C₄H₂ and C₂H₂. On another hand some C₆H₅ produced can absorb another photon and dissociate to C₄H₃ and C₂H₂ as illustrated in the reactions below.



Moreover, some •C₆H₅ produced can absorb another photon and dissociate to C₄H₃ and C₂H₂



In the study of Johnstone and Sodeau [17] performed in argon matrix at $\lambda = 253.7$ nm, benzvalene is the major photo-product. In our case in nitrogen matrix at $\lambda > 230$ nm, fulvene is the most abundant isomer. This result is not surprising since in the same study the authors had repeated the

experiment in a xenon matrix in order to investigate any “heavy atom effect” on the observed photochemistry, and no photo-products were observed. Moreover, even if benzvalene appeared first from S_1 state, it was reported that in presence of N_2 it is photolyzed in fulvene and benzene [42, 43]. While all these matrices (Ar, N_2 and Xe) crystallise in face-centered cubic lattice, the cage parameters are different and increase from Argon to Xenon (5.31 Å (Ar), 5.66 Å (N_2), 6.13 Å (Xe)) [44,45]. Therefore, the nature of the matrix has inevitably a significant impact on the quantity of the formed products. The wider the matrix is, the less it promotes isomer formation.[17]

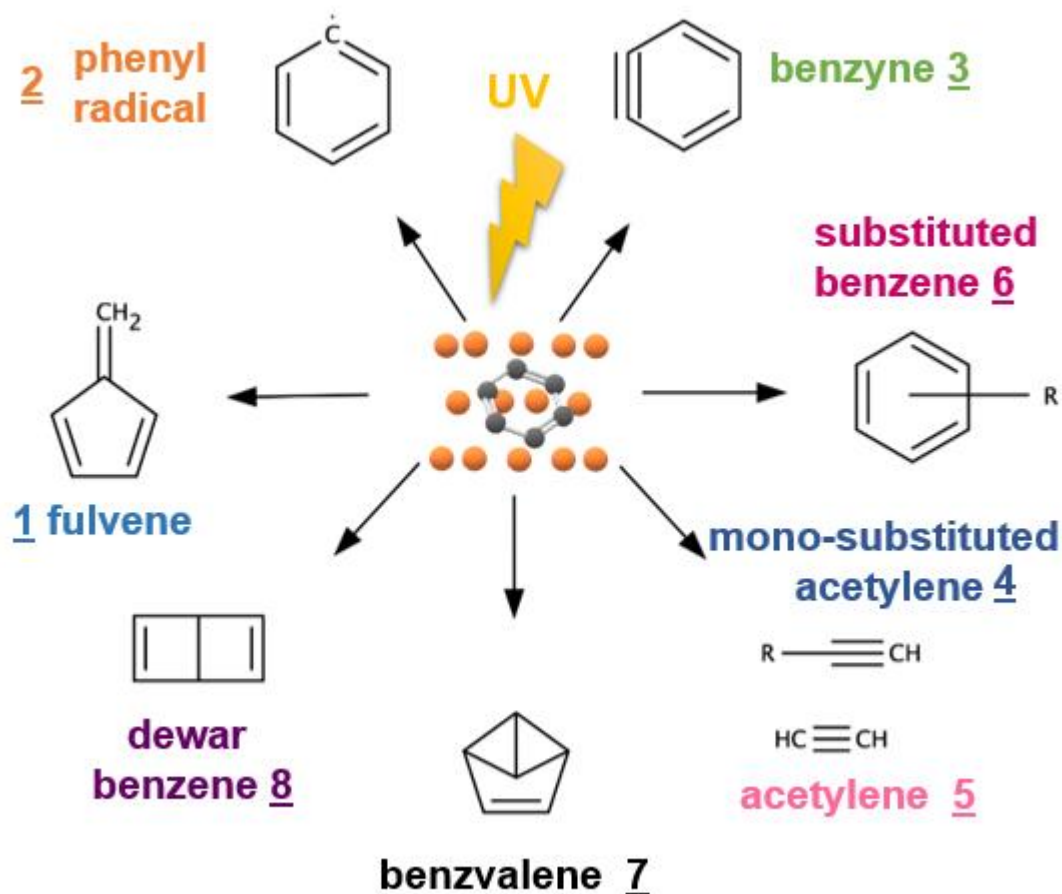
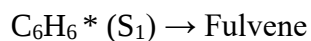
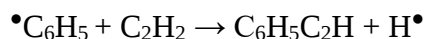


Figure 6: Main products obtained during the photolysis of benzene at $\lambda > 230$ nm

As shown in Figure 3, fulvene absorption bands increase until the end of the photolysis step in our experiment indicating that this isomer is a final product and it is most probably formed from the S_1 singlet excited state of benzene according to the reaction below[17, 21, 22].



On the other hand, phenyl radical could be considered as a reactional intermediate since it starts to slowly decrease after a little more than 500 min of photolysis (Figure 3), reflecting that it is produced as quickly as it is consumed. Thus, the phenyl radical can react with benzene or photolysis products leading to the formation of more complex molecules such as substituted benzene. This reaction has already been observed by Friderichsen et al. [30] when performing soft and short warm-up of the matrix up to 45 K. By significantly increasing the diffusion rate of phenyl radicals, the formation of substituted benzene is promoted. As mentioned in the paper of Friedrichs et al. [46] the bimolecular reaction of the phenyl radical with acetylene could yield to the phenylacetylene ($\text{C}_6\text{H}_5\text{C}_2\text{H}$) formation according to the reaction written below.



Similarly, benzyne reaches a plateau after 800 min of photolysis, suggesting that it also reacts as quickly as it is formed. Moreover, the disappearance of benzyne upon sublimation of N_2 could be explained by the recombination of two radicals to form biphenylene. The infrared spectrum calculated by Pauzat and Ellinger [47] (2002) indicates the most intense absorption band at 741 cm^{-1} (13.499 nm). Hence, the large and intense band observed at 753 cm^{-1} may be evidence of formation of a substituted benzene. On the other hand, Friedrichs et al. [46] put in evidence that the reaction between the o-benzyne and C_2H_2 could lead to the benzocyclobutadiene or phenylacetylene, two substituted benzenes.

Accordingly, the dissociation of vapour benzene may be a source of diverse volatile photoproducts in Titan's stratosphere. So far, no benzene isomers have been detected in Titan's atmosphere. As they come from the specific photochemistry of benzene and the amount of photoproducts obtained in our photolysis experiment is low, the fact that they have not yet been detected on Titan makes sense. Condensation of benzene occurs near the tropopause where the temperature diminishes. It contributes to the formation of several kind of icy clouds : one in which benzene is predominantly mixed with hydrogen cyanide [12] and another one, detected by Vinatier et al [48], at higher stratospheric altitudes (between 168 and 278 km), composed of benzene among other unassigned molecules. This shows the interest of the detection of new species in solid phase which could include products like monosubstituted acetylene, C_2H_2 aggregates and substituted benzene.

In order to determine if the photoproducts obtained during the photolysis in matrix could be formed during the direct photochemistry of the benzene ice, that we will perform in a future work, we have performed the nitrogen sublimation. The infrared spectrum obtained after this sublimation shows that fulvene is the only isomer observable in solid benzene under our experimental conditions, while others isomers are not detectable. Small amounts are probably still trapped in the solid benzene undetectable by infrared spectroscopy.

Conclusion

In this study, we have formed fulvene, phenyl and benzyne radicals and monosubstituted acetylene and substituted benzene by UV irradiation in nitrogen matrix at $\lambda > 230$ nm. After N_2 sublimation, we obtained the infrared signature of the fulvene isomer in benzene ice for the first time. Infrared band characterization of fulvene in the solid phase is very important since benzene ice has been detected in the low atmosphere of Titan. Submitted to long UV radiation, photoprocessing of this benzene cloud could result in the formation of benzene isomers in solid phase.

Acknowledgments

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