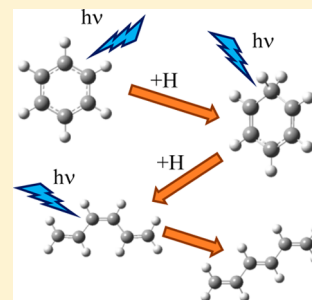


## UV Photochemistry of Benzene and Cyclohexadienyl Radical in Solid Parahydrogen

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## Supporting Information

**ABSTRACT:** Matrix-isolation spectroscopy in solid parahydrogen is a powerful technique for the study of photochemical reactions in detail. It is especially suited for the detection of chemical intermediates and unstable molecular products of photochemical reactions that are otherwise difficult to observe using other conventional spectroscopic techniques. Here, we have revisited UV photochemistry of benzene induced by 193 and 253.7 nm excitations by matrix-isolation infrared spectroscopy using solid parahydrogen as a host matrix. In addition to the formation of benzvalene, fulvene, and Dewar benzene as photoproducts of the UV photolysis of benzene, we have confirmed the production of cyclohexadienyl radical in solid parahydrogen as an intermediate species for a ring-opening reaction to 1,3,5-hexatriene. Moreover, we have identified 1,3-hexadien-5-yne and *o*-benzyne as minor products of the photochemical reaction. The reaction mechanisms of these species based on the analysis of FTIR spectra and quantum chemical calculations are discussed.

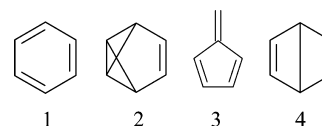


## 1. INTRODUCTION

Over the past decades, polycyclic aromatic hydrocarbons (PAHs) have been a subject of interest in astrochemical studies, as they are one of the potential candidates for the carrier of diffuse interstellar bands (DIB).<sup>1–3</sup> Understanding the UV photochemical behavior of these aromatic compounds is especially important because of the existence of strong UV radiation in the interstellar medium. Here, we have conducted UV irradiation of benzene, one of the simplest and most widely studied aromatic hydrocarbons, isolated in solid parahydrogen, aiming to expand our knowledge on the photochemical products and mechanisms of aromatic hydrocarbons.

It has been reported that photochemistry of benzene (1) in the liquid phase depends on the excitation wavelength: excitation at 254 nm to the  $S_1$  electronic excited state produces benzvalene (2) and fulvene (3),<sup>4–6</sup> and excitation at 203 nm to the  $S_2$  excited state leads to the formation of Dewar benzene (4) in addition to benzvalene and fulvene.<sup>7,8</sup> In the gas phase, the  $S_2$  excitation of benzene by 193 nm radiation produces fulvene, *cis*- and *trans*-1,3-hexadien-5-yne, and phenyl radical, but not benzvalene or Dewar benzene.<sup>9–11</sup> It was proposed that the formation of benzvalene and Dewar benzene occurs when electronically excited benzene molecules are nonradiatively deactivated into the vibrationally excited  $S_0$  state of benzene (“hot benzene”).<sup>9,12,13</sup> Efficient production of such “hot benzene” from electronically excited benzene is expected in the liquid phase via collisions, resulting in the formation of thermally unstable benzene isomers, i.e., benzvalene and Dewar benzene. In the gas phase, the nonradiative internal conversion is less efficient and therefore electronic excitation of benzene leads to the formation of thermally stable fulvene or other

photodissociated products in addition to the de-excitation to benzene itself.<sup>14</sup>



Photoexcitation products of “hot benzene” have also been investigated in the gas phase.<sup>11</sup> It was also reported that photoexcitation of vibrationally excited hot benzene leads to the production of another highly excited  $S_0$  state, resulting in the formation of cyclic  $C_6H_4$  type molecules,<sup>15,16</sup> and 1,3-hexadien-5-yne.<sup>17</sup>

Matrix-isolation spectroscopy is a powerful technique for the study of highly reactive atoms and unstable molecules, by stabilizing them in an inert solid at low temperatures.<sup>18</sup> This technique also allows for the study of light-induced chemistry, such as noble gas chemistry.<sup>19</sup> UV photolysis of benzene has been studied in Ar matrixes.<sup>20</sup> It has been reported that Dewar benzene is one of the primary products besides benzvalene and fulvene by 253 nm excitation of benzene in an Ar matrix. Theoretically, Dewar benzene is predicted to be a photoproduct of benzene via the  $S_2$  electronic excited state. Because the energy of the 253 nm radiation is not enough to excite benzene into the  $S_2$  electronic excited state, a mechanism

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involving  $S_1$ – $S_2$  state mixing induced by the matrix environment was proposed as an origin of Dewar benzene production in an Ar matrix by 253 nm excitation.<sup>20</sup> In an alternative study, various products including benzene isomers and photodissociated products were detected following 193 nm photolysis of benzene in an Ar matrix.<sup>21</sup> In that work, the authors stated that *in situ* irradiation of 193 nm did not yield any new products, but irradiation during deposition led to substantial product formation. The products they detected were produced mostly by photolysis of the benzene/Ar gas mixture during deposition that subsequently froze quickly in the cold Ar matrix. Solid Ar is known to provide a hard and bulky crystalline environment for the sample, making *in situ* photolysis difficult. Such an effect is called the “cage effect” and is considered to be one of the limitations of matrix-isolation spectroscopy.<sup>22</sup> With few exceptions, the photofragments in rare gas matrixes cannot be separated via diffusion through the matrix, so their recombination may occur more or less readily.

Quantum solid parahydrogen is a unique host material for matrix-isolation spectroscopy.<sup>23</sup> Due to a weak interaction between the parahydrogen host and the guest atoms or molecules in addition to the large amplitude of zero-point lattice vibration, parahydrogen matrixes provide a soft environment to the subject under study, resulting in weak or diminished cage effects.<sup>24–26</sup> The soft characteristic of solid parahydrogen opens up the possibility of performing *in situ* photoirradiation on the sample housed within the matrix. We have previously reported photolysis experimentations on methyl iodide,<sup>27</sup> ethyl iodide,<sup>28,29</sup> and methyl radical<sup>30,31</sup> immersed in solid parahydrogen.<sup>23</sup>

In the present study, we have reinvestigated photochemical reactions of benzene irradiated by UV photons (193 and 253.7 nm) using solid parahydrogen as a host, aiming to observe different variations in benzene photoproducts as compared to the outcomes in other matrixes.<sup>20,21</sup> The reactivity and stability of the benzene photoproducts were investigated by means of Fourier-transform infrared (FTIR) spectroscopy and density-functional theory (DFT) calculations.

## 2. EXPERIMENTAL SECTION

Benzene (Sigma-Aldrich, 99.94%) was degassed and purified by freeze–thaw cycles at 77 K and room temperature. Parahydrogen was prepared by a similar method as mentioned in previous papers.<sup>32,33</sup> Briefly, normal hydrogen gas of 99.99% purity (Praxair Canada Inc.) was converted into parahydrogen gas with a purity of 99.95%, by flowing through a magnetic catalyst (FeOH)O kept at a temperature of about 14 K. The parahydrogen gas was then mixed with 25 ppm of benzene in the gas line at room temperature. The sample mixture was introduced into a mass flow controller (STEC, SEC-4400) and was deposited onto a cold substrate (Thorlabs, Inc., ZnSe, 25.4 mm diameter, 2 mm thickness, wedged) over a period of 15 min with a flow rate of 50 ccm. The ZnSe substrate was fixed to a copper holder that was mounted on a copper cold plate. The cold plate was cooled to a temperature of 3.4 K by a closed cycle Gifford-McMahon refrigerator (Sumitomo Heavy Industries, Ltd., RDK-205D). The temperature of the cold window was about 4.2 K.

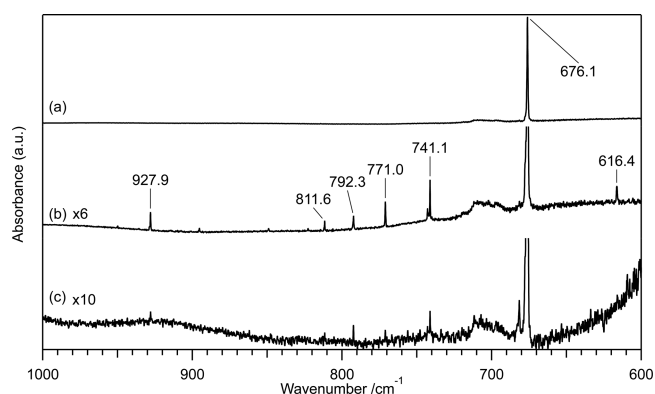
Infrared absorption spectra were taken with a Fourier-transform infrared spectrometer (Bruker, IFS 125HR) equipped with a KBr beam splitter, a liquid  $N_2$  cooled MCT detector, and a glowbar MIR light source. All the spectra were

measured at 0.2  $cm^{-1}$  resolution and averaged over 1000 scans. An ArF excimer laser (MPB PS-100, 193 nm, 5 ns, 75 Hz) and a modified low-pressure mercury vapor lamp (Regent H39KB175, 253.7 nm, 175 W, CW) were used as radiation sources for the photochemistry of benzene. Irradiation was always performed after deposition.

Density-functional theory (DFT) calculations were performed to confirm the spectral assignments in this study. The energies, vibrational wavenumbers, and IR intensities of benzene and its photochemical species were calculated using the GAUSSIAN03 program<sup>34</sup> with B3LYP/6-311+G(d, p) or B3LYP/6-311++G(2d,2p) basis sets.

## 3. RESULTS AND DISCUSSION

**3a. Main Benzene Photoproducts: Benzvalene, Fulvene, Dewar Benzene.** The infrared spectrum of benzene in solid parahydrogen is shown in Figure 1a and Figure S1



**Figure 1.** Infrared absorption spectra of benzene in solid parahydrogen at 4.2 K in the spectral region 600–1000  $cm^{-1}$ : (a) 25 ppm benzene/parahydrogen gas mixture just after deposition; (b) sample (a) after 30 min irradiation with 193 nm ArF excimer laser radiation. The spectrum is multiplied by a factor of 6; (c) sample (a) after 15 h irradiation with 253.7 nm mercury lamp radiation. The spectrum is multiplied by a factor of 10.

(Supporting Information). Three intense peaks were observed at 676.1, 1038.1, and 1482.9  $cm^{-1}$ . The most intense absorption at 676.1  $cm^{-1}$  was assigned to the C–H out-of-plane deformation mode of benzene. The absorptions at 1038.1 and 1482.9  $cm^{-1}$  were assigned to the C–H in-plane deformation and C–C deformation modes, respectively. The peak at 1009.1  $cm^{-1}$  previously reported in Ar or  $N_2$  matrixes was not detected.<sup>35,36</sup> These observed peaks showed up to 1  $cm^{-1}$  shift from the gas phase<sup>35</sup> and about 4  $cm^{-1}$  shift from Ar matrixes.<sup>36</sup> Other observed peaks of benzene, their assignments, and the associated theoretical calculated wavenumbers are summarized in Table S1 (Supporting Information).

Upon prolonged irradiation by either the 193 nm ArF excimer laser or the 253.7 nm mercury lamp, infrared absorption of benzene decreased and new bands appeared, most noticeably peaks were detected at 616.4, 741.1, 771.0, 792.3, 811.6, 895.3, and 927.9  $cm^{-1}$  (Figure 1b,c). These intense new bands were assigned to benzene isomers, namely, benzvalene, fulvene, and Dewar benzene. Our assignments of these spectral peaks were confirmed by comparing our results with previous experimental results of benzvalene, Dewar benzene<sup>37</sup> and fulvene<sup>38</sup> performed in other low-temperature matrixes or in the gas phase, as well as DFT calculated

Table 1. Observed Wavenumbers of Benzvalene, Dewar Benzene, and Fulvene in Solid Parahydrogen ( $p\text{-H}_2$ ) and in Solid Ar in Units of  $\text{cm}^{-1}$ <sup>a</sup>

benzvalene				Dewar benzene				fulvene			
$p\text{-H}_2$ <sup>b</sup>	$\text{Ar}^c$	assignment		$p\text{-H}_2$ <sup>b</sup>	$\text{Ar}^c$	assignment		$p\text{-H}_2$ <sup>b</sup>	$\text{Ar}^d$	assignment	
741.1 (1.0)	vvs	$\nu_{20}$ C—H wag.	702.2 (0.47)	705	vs	$\nu_{22}$ C—H wag.	616.4 (0.58)	613	vs	$\nu_{19}$ C—H wag.	
742.8 (0.34)	vvs			709	vs		771.0 (1.0)	769	s	$\nu_{18}$ C—H wag.	
760.4 (0.03)	mw	$\nu_{10}$ C—H wag.	792.3 (1.0)	793	vvs	$\nu_8$ C—H wag.	895.3 (0.16)	894	m	$\nu_{10}$ C—C—C str.	
811.6 (0.24)	s	$\nu_{30}$ C—C $\equiv$ C bend.		795	vvs		907.5 (0.06)	907	m	$\nu_{17}$ C—H wag.	
849.1 (0.11)	ms	$\nu_{29}$ C—H wag.	822.9 (0.22)	823	s	$\nu_{29}$ C—C str.	927.9 (0.74)	926	s	$\nu_{16}$ CH <sub>2</sub> wag.	
1089.5 (0.28)	vs	$\nu_{18}$ C—C str.		826	s		949.9 (0.07)	952	m	$\nu_9$ C—C str.	
1090.4 (0.09)	vs	$\nu_7$ C—H wag.	923.3 (0.08)	923	m	$\nu_{28}$ C—C—C bend.	1078.5 (0.09)	1077	m	$\nu_{27}$ C—H bend.	
1092.7 (0.05)	vs	$\nu_{12}$ C—H wag.	928.8 (0.41)	928	ms	$\nu_6$ C—C str.	1342.6 (0.46)	1342	s	$\nu_7$ C—H bend.	
1163.8 (0.06)	m	$\nu_6$ C—H wag.	935.4 (0.09)	936	ms	$\nu_{27}$ C—H wag.	1485.5 (0.12)	1486	s	$\nu_5$ C $\equiv$ C str.	
1182.7 (0.04)	mw	$\nu_{27}$ C—C str.		938	ms		1486.1 (0.25)				
1239.6 (0.02)	mw	$\nu_{26}$ C—C str.	1134.8 (0.11)	1135	ms	$\nu_{26}$ C—H wag.	3007.6 (0.03)	3008	s	$\nu_3$ C—H str.	
1313.3 (0.20)	m	$\nu_{25}$ C—C str.	1146.8 (0.04)	1147	ms	$\nu_4$ C—H wag.	3088.0 (0.05)	3088	m	$\nu_{22}$ C—H str.	
1554.8 (0.13)	m	$\nu_4$ C $\equiv$ C str.		1149	ms		3088.9 (0.03)			$\nu_{21}$ C—H str.	
3066.2 (0.01)	m	$\nu_{24}$ C—H str.	1268.1 (0.16)	1268	s	$\nu_{25}$ C—H wag.	3104.7 (0.01)	3104	w	$\nu_1$ C—H str.	
3071.6 (0.04)			1270	s							
			1281	m							
			1284	m							
			1535.5 (0.10)	1536	ms	$\nu_{18}$ C $\equiv$ C str.					
				1539	ms						
			2984.7 (0.05)	2986	vs	$\nu_{24}$ C—H str.					
			3048.8 (0.10)	3046	s	$\nu_2$ C—H str.					
			3058.8 (0.07)								
			3069.6 (0.15)	3069	m						
			3107.8 (0.06)	3107	m						
			3108.9 (0.05)								
			3110.9 (0.15)	3112	m	$\nu_{23}$ C—H str.					
			3111.5 (0.12)			$\nu_{17}$ C—H str.					
			3133.6 (0.06)	3134	w	$\nu_1$ C—H str.					

<sup>a</sup>Mode assignments are based on theoretical calculations. <sup>b</sup>Values in parentheses are the observed relative intensities. <sup>c</sup>Reference 37. <sup>d</sup>Reference 38.

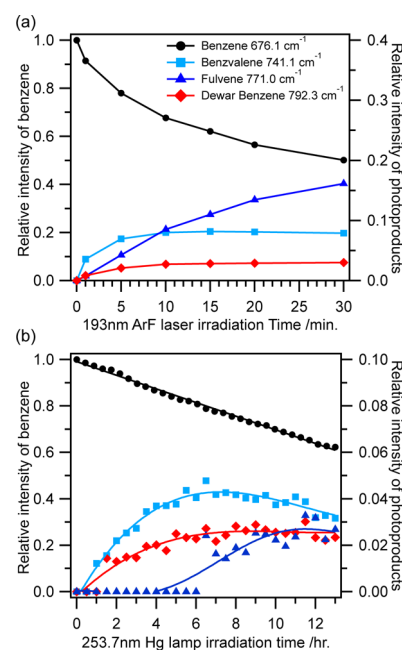
wavenumbers. In short, the absorptions at 741.1 and 811.6  $\text{cm}^{-1}$  were assigned to the C—H wagging and C=C=C bending vibrational modes of benzvalene, respectively, and the absorption at 792.3  $\text{cm}^{-1}$  was assigned to the C—H wagging mode of Dewar benzene.<sup>34</sup> The band for fulvene appeared at 616.4  $\text{cm}^{-1}$ , which was assigned to the methylene group out-of-plane bending mode, and at 771.0 and 927.9  $\text{cm}^{-1}$ , which were both assigned to the C—H out-of-plane bending modes. The absorption at 895.3  $\text{cm}^{-1}$  was assigned to the C—C—C stretching mode of fulvene.<sup>34</sup> Wavenumbers of all the bands of benzvalene, Dewar benzene, and fulvene observed in solid parahydrogen are listed in Table 1 together with those in solid Ar.<sup>37,38</sup> Complete lists of the absorptions with detailed assignments and computed values and their comparison with previously reported values in other matrixes are summarized in Table S2 for benzvalene, Table S3 for Dewar benzene, and Table S4 for fulvene (Supporting Information).

The benzene isomers, benzvalene, fulvene, and Dewar benzene, were found to be stable in solid parahydrogen. We left the resulting photoirradiated sample embedded in solid parahydrogen in the dark for 18 h at 4.2 K, but no spectral changes were detected, aside from minor matrix evaporation. This result indicates that no tunneling reaction for any isomerization nor reaction with any surrounding hydrogen molecule happened in the time scale of a day. These benzene isomers were stably trapped in solid parahydrogen and subject to further photolysis under UV irradiation.

Energetically, it is known that 193 nm radiation excites benzene into the  $S_2$  ( $^1B_{1u}$ ) electronic excited state, whereas 253.7 nm excites the molecule into the  $S_1$  ( $^1B_{2u}$ ) electronic excited state. Both 193 and 253.7 nm UV irradiation led to the production of the same three benzene isomers, but the reaction behavior of each species was different for different excitation energies. Panels a and b in Figure 2 highlight the reaction behavior displayed by changes in absorption intensities of benzene, benzvalene, fulvene, and Dewar benzene as a function of UV irradiation time.

In general, benzvalene appeared first for both 193 and 253.7 nm UV excitations, and therefore benzvalene is a primary product of photoinduced isomerization from the  $S_1$  and  $S_2$  excited states of benzene. This result matched the theoretical calculation, in which the formation of benzvalene from both the  $S_1$  and  $S_2$  excited states was predicted.<sup>39</sup> However, the increase of the benzvalene absorption did not last long for both 193 and 253.7 nm UV excitations. It was reported that the photolysis of benzvalene at 253.7 nm in the gas phase in the presence of nitrogen gas yielded a 3:1 mixture of benzene and fulvene with a quantum yield of 0.4.<sup>6,42</sup> Therefore, the decrease of benzvalene intensity suggests that benzvalene underwent secondary photoinduced reversion to benzene or isomerization/dissociation to other species after prolonged UV photolysis in solid parahydrogen.

Fulvene appeared at a slightly later irradiation time than benzvalene. By the 193 nm irradiation (Figure 2a), the fulvene intensity increased constantly over 30 min, which indicates that fulvene is the primary product of photoinduced isomerization by the 193 nm excitation, or the excitation to the  $S_2$  state. As shown in Figure 2b, fulvene appeared only after benzvalene started to decrease in the case of the 253.7 nm irradiation, which suggests that fulvene is not the primary product of photoinduced isomerization by the 253.7 nm excitation. Theoretical calculations indicate that both benzvalene and fulvene can be formed from the  $S_1$  excited state, via



**Figure 2.** Temporal behavior of the absorbance of benzene at 676.1  $\text{cm}^{-1}$  (black circle) and three benzene isomers: benzvalene at 741.1  $\text{cm}^{-1}$  (blue square), fulvene at 771.0  $\text{cm}^{-1}$  (blue triangle), and Dewar benzene at 792.3  $\text{cm}^{-1}$  (red diamond). (a) 193 nm ArF excimer laser irradiation. (b) 253.7 nm mercury lamp irradiation. The intensity of benzene was normalized to that at  $t = 0$  (left axis). The relative intensities of three benzene isomers (right axis) were obtained by normalizing them to the intensity of benzene at  $t = 0$  and using theoretically calculated intensity ratios of these isomers relative to the intensity of benzene. The calculated intensity ratios relative to benzene at 676.1  $\text{cm}^{-1}$  were 0.83 for benzvalene (741.1  $\text{cm}^{-1}$ ), 0.40 for fulvene (771.0  $\text{cm}^{-1}$ ), and 0.68 for Dewar benzene (792.3  $\text{cm}^{-1}$ ).

prefulvene.<sup>39,40</sup> In Ar matrix spectroscopy, Johnstone and Sodeau also concluded that both benzvalene and fulvene were primary products of the photolysis of benzene at 253.7 nm, although the possibility that fulvene was also produced from benzvalene could not be totally excluded.<sup>20</sup> However, the behavior shown in Figure 2b suggests that fulvene was formed via secondary photoisomerization of benzvalene in solid parahydrogen. Further evidence of this was that fulvene formation coincided with the drop in benzvalene intensity upon 253.7 nm irradiation. The direct formation of fulvene from benzene seems to be a minor process, even if it occurs in solid parahydrogen.

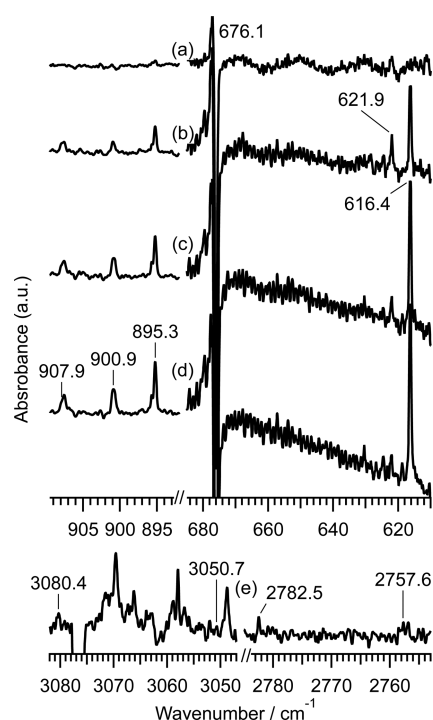
Dewar benzene was detected as a product of both the 193 and 253.7 nm UV excitations of benzene in the parahydrogen matrix. The temporal behavior was similar between the 193 and 253.7 nm excitations. No production of Dewar benzene by 253.7 nm UV irradiation was reported in the liquid<sup>4–6,41</sup> and gas phases.<sup>7–10</sup> The production of Dewar benzene was reported in Ar matrices.<sup>20,21</sup> The result in parahydrogen was the same as that reported in Ar matrixes. It was suggested that Dewar benzene forms from the  $S_2$  ( $^1B_{1u}$ ) state of benzene, but not from  $S_1$  ( $^1B_{2u}$ ) because there is a symmetry allowed pathway from the  $^1B_{1u}$  state but not from the  $^1B_{2u}$  state.<sup>14</sup> However, it was also suggested that the electronic symmetry-allowed process from the  $^1B_{1u}$  state to the excited state of Dewar benzene is energetically forbidden.<sup>42</sup> The formation mechanism of Dewar benzene is still under debate, but the production of Dewar benzene from both the  $S_1$  and  $S_2$  excited states in parahydrogen



implies that a vibronic mechanism involving nonradiative relaxation to highly vibrational excited states in the  $S_0$  state of benzene is responsible for the formation of Dewar benzene.

The absorption intensity of Dewar benzene became almost constant after some period of UV irradiation for both 193 and 253.7 nm. It was reported that photoexcitation of Dewar benzene resulted in the back-conversion to benzene with the quantum yield of more than 0.9.<sup>42</sup> The observed evidence that the absorption intensity of Dewar benzene became constant after prolonged UV photolysis indicates that there is an equilibrium between benzene and Dewar benzene in a parahydrogen matrix.

**3b. Formation and Reaction of Cyclohexadienyl Radical.** Figure 3 shows the subtracted infrared spectra of



**Figure 3.** Subtracted infrared spectra of benzene in solid parahydrogen at 4.2 K at different irradiation times with 193 nm ArF laser irradiation. The spectrum recorded at deposition was subtracted out of each spectra taken after varying UV irradiation time: (a) 1 min; (b) 10 min; (c) 20 min; (d) 30 min. The concentration of benzene was 25 ppm relative to parahydrogen. The peak assignments are fulvene ( $616.4\text{ cm}^{-1}$ ),  $c\text{-C}_6\text{H}_7$  ( $621.9\text{ cm}^{-1}$ ), benzene ( $676.1\text{ cm}^{-1}$ ), fulvene ( $895.3\text{ cm}^{-1}$ ), *trans*-1,3,5-hexatriene ( $900.9\text{ cm}^{-1}$ ), and *cis*-1,3,5-hexatriene (*E*) ( $907.9\text{ cm}^{-1}$ ). Bottom panel (e): difference spectrum in the ranges 2750–2785 and 3040–3090  $\text{cm}^{-1}$  obtained by subtracting the spectrum acquired immediately after deposition from the spectrum after 10 min UV irradiation (corresponding to (b)).

benzene embedded in solid parahydrogen at different irradiation times with 193 nm UV radiation (Figure 3a, 1 min; Figure 3b, 10 min; Figure 3c, 20 min; Figure 3d, 30 min). All traces were obtained by subtracting the spectrum observed immediately after the deposition from the corresponding UV irradiated spectra. Aside from the fulvene peaks at  $616.4$  and  $895.3\text{ cm}^{-1}$ , we have also observed the appearance of several new bands upon irradiation at 193 nm. One noticeable peak was at  $621.9\text{ cm}^{-1}$ , which appeared only at very early times (within a few minutes) of the 193 nm UV irradiation as shown in Figure 3a,b.

A possible assignment to this new peak at  $621.9\text{ cm}^{-1}$  would be cyclohexadiene ( $\text{C}_6\text{H}_8$ ), which could be produced by the reaction between excited benzene and a hydrogen molecule from the surrounding environment. Cyclohexadiene exists in two isomer forms. 1,3-Cyclohexadiene shows a strong peak at  $658\text{ cm}^{-1}$  in Ar matrixes,<sup>43</sup> whereas 1,4-cyclohexadiene possesses a peak at  $622\text{ cm}^{-1}$  in 10%  $\text{CS}_2$  solution and  $625\text{ cm}^{-1}$  in vapor phase.<sup>44</sup> The latter absorption is very close to  $621.9\text{ cm}^{-1}$  as shown in Figure 3b. To check the possibility of cyclohexadiene as a carrier of this new peak, we have carried out a separate experiment, in which we deposited both 1,3- and 1,4-cyclohexadienes in solid parahydrogen and obtained the FTIR spectra. The observed spectra showed an absorption peak of 1,4-cyclohexadiene at  $620.8\text{ cm}^{-1}$ , and an absorption peak of 1,3-cyclohexadiene at  $660.1\text{ cm}^{-1}$ .<sup>45</sup> These peaks do not match the position of the new peak at  $621.9\text{ cm}^{-1}$ . Furthermore, we did not observe these cyclohexadiene peaks at any point during UV irradiation time. Therefore, it is concluded that cyclohexadiene is not a photoproduct of benzene photolysis in solid parahydrogen, nor the carrier of the peak at  $621.9\text{ cm}^{-1}$ .

Cyclohexadienyl radical ( $c\text{-C}_6\text{H}_7$ ) is another candidate molecule, which is a hydrogen atom adduct of benzene. Infrared spectra of  $c\text{-C}_6\text{H}_7$  in solid parahydrogen were reported recently, which showed a strong peak at  $622.0\text{ cm}^{-1}$  and were assigned to the  $\nu_{21}$  band of the sample molecule.<sup>46</sup> The observed peak at  $621.9\text{ cm}^{-1}$  shown in Figure 3b matches to the reported value within our instrumental resolution. In addition, we have observed four other weak peaks that showed the same irradiation behavior as the peak at  $621.9\text{ cm}^{-1}$ , which are shown in Figure 3e. The observed peaks are summarized in Table 2

**Table 2.** Observed Wavenumbers ( $\text{cm}^{-1}$ ) and Relative Intensities of Cyclohexadienyl Radical ( $c\text{-C}_6\text{H}_7$ ) Produced by 193 nm UV Photolysis of Benzene in Solid Parahydrogen

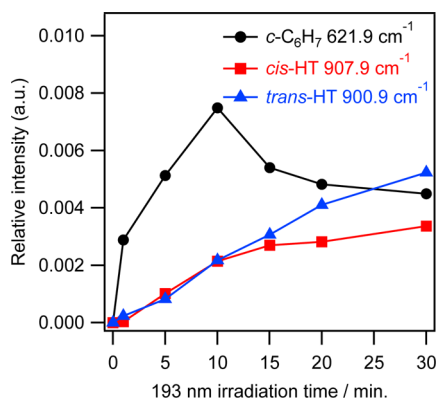
mode		para- $\text{H}_2^a$	para- $\text{H}_2^c$	theory <sup>c</sup>
$\nu_{22}$	$b_1$		510.2 (11)	518 (12)
$\nu_{21}$	$b_1$	621.9 (100) <sup>b</sup>	622 (100)	625 (100)
$\nu_{11}$	$a_1$		864.1 (3)	867 (4)
$\nu_{19}$	$b_1$		910.7 (7)	909 (9)
$\nu_{10}$	$a_1$		959.8 (5)	959 (6)
$\nu_{18}$	$b_1$		970.5 (1)	977 (1)
$\nu_{29}$	$b_2$		1289.9 (4)	1284 (8)
$\nu_{27}$	$b_2$		1389.7 (1)	1387 (1)
$\nu_7$	$a_1$		1394.7 (9)	1405 (8)
$\nu_6$	$a_1$		1425.6 (5)	1424 (5)
$\nu_{17}$	$b_1$	2757.6 (9)	2757.4 (10)	2755 (20)
$\nu_4$	$a_1$	2782.5 (15)	2780.1 (23)	2763 (52)
$\nu_2$	$a_1$		3030.5 (3)	3035 (4)
$\nu_3$	$a_1$	3050.7 (4)	3050 (10)	3049 (9)
$\nu_{24}$	$(b_2)$		3056.8? (14)	3030 (51)
$\nu_1$	$(a_1)$	3080.4 (10)	3080.4 (13)	3071 (14)

<sup>a</sup>Values obtained by the present study. <sup>b</sup>Observed intensities listed in parentheses were normalized to the most intense band of  $c\text{-C}_6\text{H}_7$  at  $621.9\text{ cm}^{-1}$ . <sup>c</sup>Reference 46.

together with the corresponding reported  $c\text{-C}_6\text{H}_7$  peaks in solid parahydrogen. All of these new peaks are in good agreement with the reported absorption peaks of  $c\text{-C}_6\text{H}_7$  in solid parahydrogen. Hence, we conclude that the  $621.9\text{ cm}^{-1}$  peak that appeared during the early stage of 193 nm irradiation is assigned to  $c\text{-C}_6\text{H}_7$ .

$c\text{-C}_6\text{H}_7$  has been a subject of interest in spectroscopic studies due to its essential role as an intermediate for the hydrogenation process of aromatic hydrocarbons in both gas and condensed phases.<sup>47–49</sup> One of the first matrix-isolation spectroscopy experiments on  $c\text{-C}_6\text{H}_7$  was done by Andrews and his group who have recorded UV–vis spectra of the radical in Ar matrixes.<sup>50</sup> Recently, Feldman's group has recorded the IR and EPR spectra of  $c\text{-C}_6\text{H}_7$  embedded in solid Xe,<sup>51</sup> whereas another group by Lee has performed IR measurements on the radical and its deuterated species,  $c\text{-C}_6\text{D}_7$ , in solid parahydrogen at 3.2 K.<sup>46</sup> Feldman's group used fast electron irradiation of benzene for the production of  $c\text{-C}_6\text{H}_7$ , whereas Lee's group used an electron bombardment method. Electron bombardment of parahydrogen gas prior to deposition led to the formation of  $\text{H}_3^+$ , which then reacted with benzene to form protonated benzene ( $\text{C}_6\text{H}_7^+$ ), and the protonated benzene was subsequently neutralized into  $c\text{-C}_6\text{H}_7$ .<sup>28,46</sup> In our experiment, it is not likely that *in situ* 193 nm irradiation of solid parahydrogen produced  $\text{H}_3^+$ , because three photons at 193 nm are necessary to ionize  $\text{H}_2$ , whereas we did not focus the 193 nm pulses for the UV irradiation. Therefore,  $\text{H}_3^+$  or any other ions cannot be an intermediate to produce  $c\text{-C}_6\text{H}_7$  as in the previous works. It is known that hydrogen atoms are produced by the 193 nm irradiation of doped hydrogen crystals, which diffuse in parahydrogen crystals.<sup>52</sup>  $c\text{-C}_6\text{H}_7$  in this experiment must be produced by the neutral–neutral reaction between benzene and an H atom.

As highlighted in Figure 3,  $c\text{-C}_6\text{H}_7$  was detected only at the beginning of the 193 nm UV irradiation. The absorption at  $621.9\text{ cm}^{-1}$  became weak after 30 min of irradiation, while other benzene isomers still survived (Figure 3c). The decrease of the peaks corresponding to  $c\text{-C}_6\text{H}_7$  must be due to the secondary photolysis of  $c\text{-C}_6\text{H}_7$  by the 193 nm UV irradiation. We noticed that new peaks appeared at 900.9, 907.9, 990.6, and  $1012.02\text{ cm}^{-1}$  when the peak of  $c\text{-C}_6\text{H}_7$  started to decrease (Figure 3d for the spectral range of  $890\text{--}910\text{ cm}^{-1}$ ). The temporal behavior of the peaks at 900.9 and  $907.9\text{ cm}^{-1}$  is shown in Figure 4 together with that of  $c\text{-C}_6\text{H}_7$  at  $621.9\text{ cm}^{-1}$ , which suggests that these new peaks can be assigned to the products of  $c\text{-C}_6\text{H}_7$  photolysis. The peak at  $990.6\text{ cm}^{-1}$  behaved similarly to the peak at  $900.9\text{ cm}^{-1}$ , and the peak at  $907.9\text{ cm}^{-1}$  behaved similarly to the peak at  $1012.02\text{ cm}^{-1}$ .



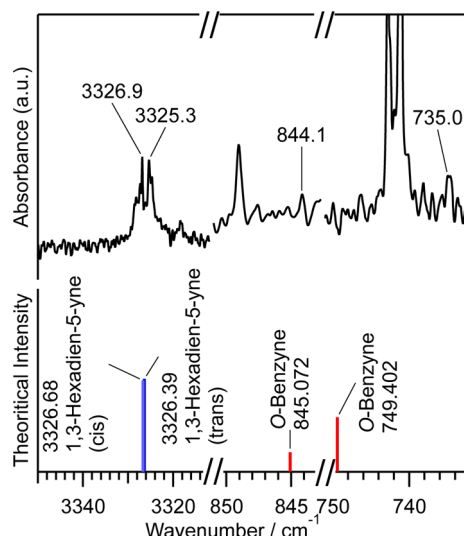
**Figure 4.** Temporal behavior of the intensity of  $c\text{-C}_6\text{H}_7$  at  $621.9\text{ cm}^{-1}$  (black circle), *cis*-hexatriene (*cis*-HT) at  $907.9\text{ cm}^{-1}$  (red square), and *trans*-hexatriene (*trans*-HT) at  $900.9\text{ cm}^{-1}$  (blue triangle) by 193 nm ArF irradiation. The relative intensities of  $c\text{-C}_6\text{H}_7$  and *trans*- and *cis*-1,3,5-hexatriene were obtained by normalizing them to the intensity of benzene at  $t = 0$ .

1,3,5-Hexatriene is known to be formed by strong UV irradiation of benzene solution in rigid glass at liquid air temperature when the solvent contains hydrogen.<sup>53</sup> This molecule has two separable stable isomers, namely (*E*)-1,3,5-hexatriene (or *trans*-hexatriene) and (*Z*)-1,3,5-hexatriene (or *cis*-hexatriene). In solid Ar matrixes, *trans*-hexatriene showed strong IR vibrational peaks at  $899$  and  $1012\text{ cm}^{-1}$ , whereas *cis*-hexatriene showed peaks at  $906$  and  $987\text{ cm}^{-1}$ .<sup>54</sup> These reported values matched the observed peak values. Consequently, we have assigned the new photochemical products as *trans*-hexatriene and *cis*-hexatriene. A full list of vibrational wavenumbers of *cis*- and *trans*-hexatriene in solid parahydrogen and comparison with reported wavenumbers in other matrixes and calculated values is given in Tables S5 and S6 (Supporting Information). According to previous studies, the formation process of 1,3,5-hexatriene via benzene UV photolysis goes through the intermediate 1,3-cyclohexadiene.<sup>55,56</sup> However, 1,3-cyclohexadiene was not detected in our experiment at any irradiation time. Therefore, the generation of 1,3,5-hexatriene under the present condition must involve a new mechanism with  $c\text{-C}_6\text{H}_7$  radical as a reaction intermediate.

It was reported that UV photolysis of  $c\text{-C}_6\text{H}_7$  by a medium pressure Hg lamp produced open-chain molecules (*E*)-1,4,5-hexatrien-3-ylidene (E-HT) and  $\alpha$ -hydrogenated fulvene ( $\alpha$ -HF) in solid neon matrixes.<sup>57</sup> DFT calculations showed that E-HT must have two strong IR absorptions at  $865.5\text{ cm}^{-1}$  ( $\nu_{18}$ ) and  $835.8\text{ cm}^{-1}$  ( $\nu_{27}$ ), corresponding to the  $\text{CH}_2$  out-of-plane deformation of allene group and C–H out-of-plane deformation of ethyl group, respectively (Table S7, Supporting Information), whereas  $\alpha$ -HF must have an intense vibrational peak at  $806.0\text{ cm}^{-1}$  ( $\nu_{27}$ ), corresponding to the C–H bending of the ethyl group (Table S8, Supporting Information). The new peaks observed at  $900.9$ ,  $907.9$ ,  $990.6$ , and  $1012.02\text{ cm}^{-1}$  do not match with these calculated values. Therefore, we conclude that neither E-HT nor  $\alpha$ -HF is a photochemical product of  $c\text{-C}_6\text{H}_7$  in parahydrogen matrixes.

**3c. Minor Photoproducts.** In addition to the peaks previously discussed, we have observed weak intensity peaks at  $3326.9$  and  $3325.5\text{ cm}^{-1}$  due to 193 nm irradiation of benzene in solid parahydrogen (Figure 5). These peaks were observed shortly after fulvene started to appear. Other peaks were also observed at  $624.58$ ,  $630.43$ ,  $914.34$ ,  $923.25$ ,  $1014$ ,  $3327.3$ , and  $3325.3\text{ cm}^{-1}$  at the same time. On the basis of the reported gas phase values,<sup>58</sup> these peaks were assigned to absorptions of 1,3-hexadien-5-yne. Indeed, it was reported that 1,3-hexadien-5-yne was produced by the photoirradiation process of fulvene at  $185\text{ nm}$ ,<sup>10</sup> which also supports the present assignments. As listed in Table S9 (Supporting Information), the calculated frequencies and intensities indicate that the peaks at  $630.43$ ,  $923.25$ ,  $3326.9$ , and  $3327.3\text{ cm}^{-1}$  can be assigned to *cis*-1,3-hexadien-5-yne, whereas the peaks  $624.58$ ,  $914.34$ ,  $1014$ ,  $3324.7$ , and  $3325.3\text{ cm}^{-1}$  can be assigned to *trans*-1,3-hexadien-5-yne.

Two other peaks at  $735$  and  $844\text{ cm}^{-1}$  were also detected after 193 nm irradiation of benzene (Figure 5). These peaks were assigned to the CH wagging and ring deformations, respectively, of *o*-benzyne.<sup>59</sup> A full list of vibrational wavenumbers of *o*-benzyne in solid parahydrogen and comparisons with reported wavenumbers in other matrixes and calculated values is given in Table S10 (Supporting Information). In gas phase UV photolysis, the elimination of two hydrogen atoms from vibrational excited benzene to form cyclic  $\text{C}_6\text{H}_4$  molecular species were reported.<sup>15,16</sup> Three benzyne isomers, *o*-benzyne, *m*-benzyne, and *p*-benzyne, have been observed in low-



**Figure 5.** (Top) absorption spectrum after 30 min irradiation with 193 nm ArF laser pulses. New peaks at 735.0, 844.1, 3325.3, and 3326.9  $\text{cm}^{-1}$  were observed. The strong absorptions at 741.1 and 742.8  $\text{cm}^{-1}$  are due to benzvalene. (Bottom) theoretically predicted vibrational wavenumbers of *o*-benzynes (749.402 and 845.072  $\text{cm}^{-1}$ ), 1,3-hexadien-5-yne (*cis*) (3326.68  $\text{cm}^{-1}$ ), and 1,3-hexadien-5-yne (*trans*) (3326.39  $\text{cm}^{-1}$ ) obtained by the B3LYP/6-311+G(d, p) method.

temperature matrixes as products of UV photoirradiation of their precursor molecules.<sup>59–65</sup> *o*-Benzynes in an Ar matrix showed the most intense peak at 472  $\text{cm}^{-1}$  and medium intensity peaks at 737 and 849  $\text{cm}^{-1}$ .<sup>59</sup> The observed peaks at 735 and 844  $\text{cm}^{-1}$  match these medium intensity peaks in the Ar matrix. In addition, a weak peak was detected at 1057  $\text{cm}^{-1}$  in solid parahydrogen, which also matches the peak of *o*-benzynes at 1055  $\text{cm}^{-1}$  observed in solid Ar.<sup>59</sup> *m*-Benzynes in an Ar matrix showed the most intense peak at 547  $\text{cm}^{-1}$ , and medium intensity peaks at 751 and 824  $\text{cm}^{-1}$ .<sup>64</sup> *p*-Benzynes in a Ne matrix showed the most intense peak at 758  $\text{cm}^{-1}$ .<sup>65</sup> Peaks corresponding to these absorptions of *m*-benzynes and *p*-benzynes were not detected in the present parahydrogen matrix. It is reported that *o*-benzynes is the most stable molecule of these three benzyne isomers.<sup>66</sup> In solid parahydrogen, the most stable *o*-benzynes seemed to be detected as a photoproduct of benzene, although the detected peak intensities were extremely weak.

It has been reported that the elimination of two hydrogen atoms to produce benzyne ( $\text{C}_6\text{H}_4$ ) takes place via two-photon dissociation at 193 nm.<sup>16</sup> Because the absorption peaks at 735 and 844  $\text{cm}^{-1}$  were weak, we are not certain at this moment if *o*-benzynes is produced by a two-photon cascade excitation via “hot-benzene” due to a single 193 nm pulse or some other reaction mechanism. It has also been reported that two ring-opening dissociation channels, resulting in  $\text{C}_5\text{H}_3 + \text{CH}_3$  and  $\text{C}_4\text{H}_3 + \text{C}_2\text{H}_3$ , occur via two-photon dissociation at 193 nm.<sup>16</sup> We did not observe any absorption of  $\text{CH}_3$ <sup>27,67</sup> or  $\text{CH}_4$ <sup>68</sup> as products of *in situ* 193 nm photolysis of benzene in parahydrogen. Further investigation is necessary such as measurements of irradiation power dependence to understand the role of “hot-benzene” during UV photolysis in parahydrogen matrixes. Nevertheless, we believe that this is the first report of *o*-benzynes produced by direct photolysis of benzene in cryogenic matrixes.

## 4. CONCLUSIONS

In this study, we have detected three benzene isomers, benzvalene, fulvene, and Dewar benzene, and several other products by the *in situ* UV photolysis of benzene isolated in solid parahydrogen. All three benzene isomers were detected as the primary photoproducts by the excitation to the  $\text{S}_2$  state of benzene by 193 nm UV radiation. The excitation to the  $\text{S}_1$  state of benzene by 253.7 nm UV radiation resulted in the production of only benzvalene and Dewar benzene. Fulvene seemed to be formed solely from the photoisomerization of benzvalene by 253.7 nm UV radiation. Aside from these benzene isomers, we have also observed the formation of cyclohexadienyl radical ( $\text{c-C}_6\text{H}_7$ ) by 193 nm UV photolysis of benzene in solid parahydrogen. The cyclohexadienyl radical must be produced without having any protonated ions as an intermediate. The produced cyclohexadienyl radical subsequently underwent a ring-opening mechanism to produce 1,3,5-hexatriene after prolonged 193 nm UV irradiation. Finally, we have confirmed the detection of the minor benzene photoproducts 1,3-hexadien-5-yne and *o*-benzynes by the 193 nm irradiation. A variety of molecules were detected as a result of the *in situ* UV photolysis of benzene by virtue of the weak cage effect of solid parahydrogen.

## ■ ASSOCIATED CONTENT

### Supporting Information

Full infrared spectra of benzene in solid parahydrogen, spectral change of benzene in solid parahydrogen under 193 nm irradiation in the IR regions 600–1020 and 1010–1060  $\text{cm}^{-1}$ , spectral change of benzene in solid parahydrogen under 253.7 nm irradiation in the IR region of 600–900  $\text{cm}^{-1}$ , full lists of observed wavenumbers of benzene, fulvene, Dewar benzene, and benzvalene compared with those in other matrixes and theoretical calculations, full lists of observed wavenumbers of vibrational wavenumbers of 3-*cis*-1,3,5-hexatriene and 3-*trans*-1,3,5-hexatriene compared with those in other matrixes and theoretical calculations, calculated vibrational wavenumbers of (*E*)- and (*Z*)-1,4,5-hexatriene-3-ylidene,  $\alpha$ - and  $\beta$ -hydrogenated fulvene, and full lists of observed wavenumbers of 1,3-hexatriene-5-yne and *o*-benzynes in solid parahydrogen compared with those in other matrixes and theoretical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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