

MATRIX ISOLATION STUDY OF THE 193 nm EXCIMER LASER PHOTOCHEMISTRY OF HEXAFLUOROBENZENE

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193 nm excimer laser irradiation of Ar/C₆F₆ samples during deposition onto a cryogenic surface has led to the formation and isolation of a range of products, the dominant being hexafluoro-Dewar benzene. Additional absorptions likely due to the previously unreported hexafluorobenzvalene were observed, along with extensive fragmentation and additional minor products. When either Cl₂ or CCl₄ was doped into the Ar/C₆F₆ sample as an electron trap, a number of additional product bands were noted. A few of these were destroyed by subsequent Hg arc irradiation, and at least one is tentatively assigned to the C₆F₆⁺ cation. A comparison to previous studies of the photochemistry of C₆F₆ is made.

KEY WORDS: Matrix isolation, photochemistry, intermediates

INTRODUCTION

The identification of intermediates in photochemical processes is important in understanding the dynamics of excited states of molecules. Since many of these intermediates are very short-lived, transient techniques have been employed on a number of occasions. Alternatively, trapping of initial photochemical products into argon matrices may isolate and preserve these species for spectroscopic study.¹ While this approach has been exploited on many occasions, the advent of the excimer laser has increased the range of accessible species.

In a recent study in this laboratory, the photochemistry of benzene after irradiation with the 193 nm ArF laser line was reported.² Both isomerization and fragmentation products were observed, in a ratio that was dependent on the concentration of the precursor in the matrix. Hexafluorobenzene provides an interesting contrast to benzene, as a consequence of the stronger C—F bond. Also, while several isomers of C₆F₆ are well known, much less is known about the isomeric forms of C₆F₆. Only hexafluoro Dewar benzene has been reported,³ while very little is known about the hexafluorobenzvalene, prismane or fulvene isomers. In addition, while C₆F₆ has been the object of several photochemical studies,^{3,4} these have not been at 193 nm, where C₆F₆ is known to absorb strongly.⁵ Also, while the gas phase photochemistry of C₆F₆ has been examined, matrix trapping of intermediates has not been attempted to date.

Finally, the photoelectron transitions for hexafluorobenzene occur⁶ at 9.8–10.8, 12.5–13.5 and 16.0 eV. Thus, two-photon ionization to form the radical cation is possible provided a suitable electron trap is present in the matrix. With these considerations in mind, a study was undertaken to examine the argon matrix-isolated products of the 193 nm excimer laser irradiation of Ar/C₆F₆ samples, with and without an added electron trap.

EXPERIMENTAL SECTION

The experiments in this study were carried out on conventional matrix isolation equipment that has been described.^{2,7,8} Briefly, gas samples containing C₆F₆ (Aldrich) were deposited onto a CsI cold window maintained at 14 K. Some samples were doped with either Cl₂ (Matheson) or CCl₄ (MCB Reagents). The reagents were purified by repeated freeze-pump-thaw cycles at 77 K prior to sample preparation. Samples were deposited for 20–24 hours before final spectra were recorded from 400 to 4000 cm⁻¹ on a Mattson Cygnus Fourier transform infrared spectrometer at 1 cm⁻¹ resolution. Two arrangements were used for irradiation of the sample by a Lambda Physik EMG 103 MSC excimer laser operating at 193 nm. In the first (in situ), the sample was deposited, the deposition stopped and the final (pre-irradiation) spectra recorded. The cold window was then rotated by 45 degrees, allowing exposure to the laser beam through a suprasil window. The sample was irradiated for 1–2 hours, after which the cold window was rotated back into the beam of the spectrometer, and additional spectra were recorded. In the second, the cold window was rotated at the beginning of the experiment, and irradiation was concurrent with deposition. In both arrangements, the laser repetition rate was 5 Hz, with a pulse duration of 10 ns and a pulse energy up to 200 mJ.

RESULTS

Prior to irradiation experiments, blank experiments were carried out for each of the parent species. The spectra obtained in these blanks were in very good agreement with literature spectra.^{9–11} In some of the later experiments, CH₄ was observed as a minor impurity arising from the walls of the vacuum system.

Several initial experiments were carried out irradiating Ar/C₆F₆ and Ar/C₆F₆/Cl₂ samples in situ. No product absorptions were noted in any of these experiments. Consequently, in situ irradiation was abandoned, and all subsequent experiments were carried with irradiation concurrent with deposition.

A number of experiments were conducted in which samples of Ar/C₆F₆ were irradiated during deposition with the excimer laser. In these experiments, a large number of new infrared absorptions were observed, (see Table 1 and Figures 1 and 2) for typical experiments with concentrations of 1000/1 and 500/1. Over the series of experiments, these bands were observed reproducibly.

Table 1 Band Positions (cm^{-1}) and Assignments for the Products of the Excimer-Laser Irradiation of C_6F_6 in Argon Matrices

<i>Band</i>	<i>Ar/C₆F₆ =</i>		<i>Assignment</i>
	<i>500/1</i>	<i>1000/1</i>	
1772	0.079	0.047	1,4-cyclo- C_6F_8
1751	0.759	0.296	Hexafluoro Dewar-benzene
1740	0.034	0.024	1,3-cyclo- C_6F_8
1733	0.028	0.026	1,4-cyclo- C_6F_8
1722	0.294	0.093	$\text{C}_6\text{F}_5\text{H}$
1717	sh	0.054	1,3-cyclo- C_6F_8
1715	sh	0.051	1,3-cyclo- C_6F_8
1704	0.123	0.058	
1700	0.118	0.063	
1677	0.100	0.047	Hexafluorobenzvalene
1623	0.134	0.084	
1617	0.026	0.153	
1608	0.079	0.113	
1599 ^a	0.203	0.116	Hexafluorobenzvalene
1542	0.316	0.263	$\text{C}_6\text{F}_5\text{H}$
1512	0.368	0.118	$\text{C}_6\text{F}_5\text{H}$
1501	0.326	0.111	$\text{C}_6\text{F}_5\text{CH}_3/\text{C}_{12}\text{F}_{10}$
1428	0.403	0.147	$\text{C}_6\text{F}_5\text{CF}_3$
1424	0.465	0.169	$\text{C}_6\text{F}_5\text{CF}_3$
1411	0.323	0.110	$\text{C}_6\text{F}_5\text{H}$
1358 ^a	0.661	0.447	$\text{C}_6\text{F}_5\text{CF}_3$
1341	0.142	0.077	Hexafluoro Dewar-benzene
1327	0.103	0.030	C_2F_4
1311	0.195	0.092	C_6F_{10}
1268	0.051	0.019	Hexafluoro Dewar-benzene
1230	0.068	0.010	Hexafluoro Dewar-benzene
1184	0.099	0.032	C_2F_4
1132	0.063	0.013	$\text{C}_6\text{F}_5\text{CH}_3$
1103	0.068	0.021	CF_3CCF
1080	0.126	0.025	Hexafluoro Dewar-benzene/ $\text{C}_{12}\text{F}_{10}$
1074	0.101	0.030	$\text{C}_6\text{F}_5\text{H}$
1065	0.136	0.023	$\text{F}(\text{CC})_2\text{F}$
1057	0.189	0.053	$\text{C}_6\text{F}_5\text{H}$
1010	sh	sh	$\text{C}_6\text{F}_5\text{CF}_3$
994	sh	sh	C_6F_{10}
990	sh	sh	C_2F_4
986	sh	sh	$\text{C}_{12}\text{F}_{10}$
980	0.142	0.048	$\text{C}_6\text{F}_5\text{H}$
972	0.191	0.047	$\text{C}_6\text{F}_5\text{H}$
963	0.037	0.026	$\text{C}_6\text{F}_5\text{H}$
958	0.032	...	$\text{C}_6\text{F}_5\text{CH}_3$
953	0.042	0.021	$\text{C}_6\text{F}_5\text{H}$
947	0.026	0.021	
938	0.021	0.008	$\text{C}_6\text{F}_5\text{CH}_3$
926	0.656	0.254	Hexafluoro Dewar-benzene
884	0.050	0.032	Hexafluoro Dewar-benzene
675	...	0.093	

^aPresent at lower intensity in experiments without irradiation.

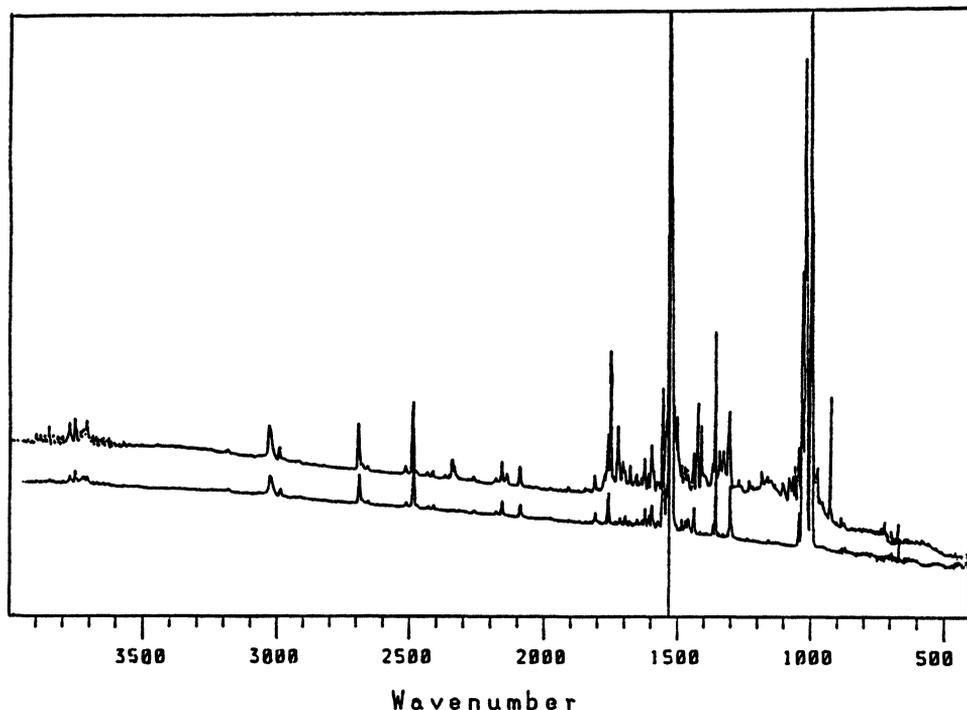


Figure 1 Infrared spectra, from 400 to 4000 cm^{-1} , of a sample of $\text{Ar}/\text{C}_6\text{F}_6 = 500$ subjected to 193 nm excimer laser irradiation during deposition (upper trace) compared to a spectrum of a similar sample without irradiation (lower trace).

In a second set of experiments, samples of $\text{Ar}/\text{C}_6\text{F}_6/\text{CCl}_4$ were irradiated during deposition, at several different concentration ratios. In these experiments, many new product absorptions were noted, as listed in Table 2. A number of these coincide with product absorptions observed above when C_6F_6 was irradiated, although with diminished intensity. Several bands match those observed during the irradiation of blank samples of Ar/CCl_4 , while yet additional bands were new and required the presence of both precursors. Two of these matrix samples were subsequently subjected to irradiation from a medium pressure Hg arc lamp. As also noted in Table 2, some of the product bands were reduced in intensity or destroyed by Hg lamp irradiation.

Samples of $\text{Ar}/\text{C}_6\text{F}_6/\text{Cl}_2$ were irradiated during deposition in a third set of experiments, at several different concentration ratios. As in the above experiments, a large number of new infrared absorptions were observed in these experiments, the majority of which corresponded to bands seen in the $\text{Ar}/\text{C}_6\text{F}_6/\text{CCl}_4$ experiments. All of the product bands in the $\text{Ar}/\text{C}_6\text{F}_6/\text{Cl}_2$ system are listed in Table 3. One of these matrices was then subjected to Hg arc irradiation; as also shown in Table 3, several of the product bands were reduced or destroyed by the Hg arc.

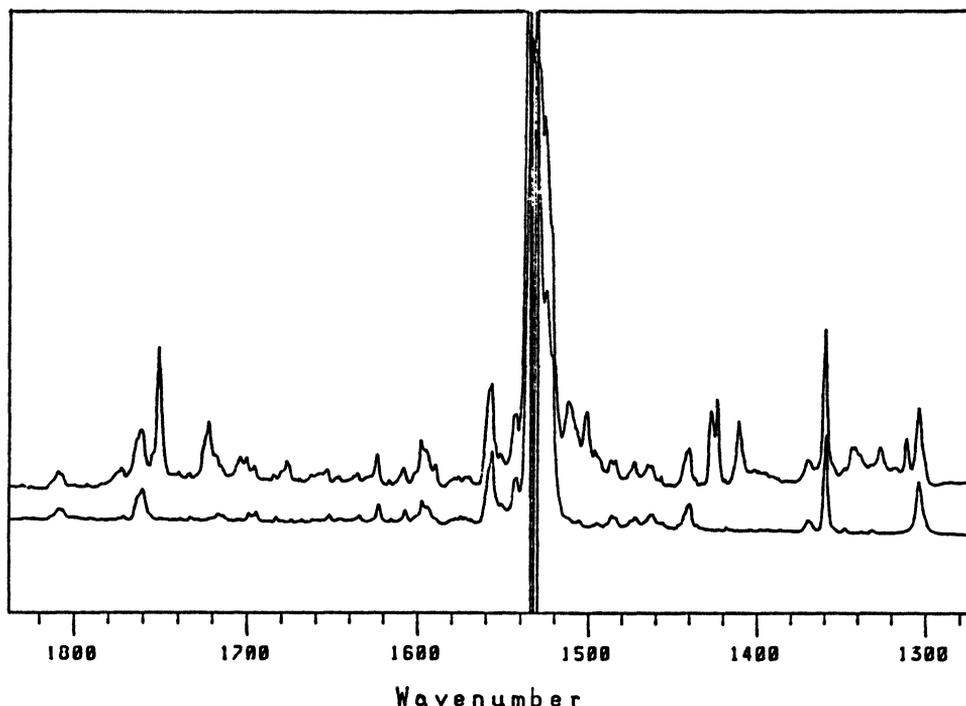


Figure 2 Infrared spectra, from 1270–1840 cm^{-1} , of a sample of $\text{Ar}/\text{C}_6\text{F}_6 = 500$ subjected to 193 nm excimer laser irradiation during deposition (upper trace) compared to a spectrum of a similar sample without irradiation (lower trace).

DISCUSSION

Product Identification

As is apparent from Tables 1–3, numerous new absorptions were seen following 193 nm excimer laser irradiation with or without added dopant. Previous studies² have demonstrated that even with the short time between irradiation and matrix trapping there is sufficient time for extensive reaction and rearrangements to occur. As a consequence, radicals are not commonly isolated as they react and recombine rapidly. The literature, then, was searched in an attempt to match the many new absorptions to known fluorocarbons, matching both band position and relative intensities to spectra of known compounds. Unfortunately, the infrared spectrum of only two isomers of C_6F_6 itself are known, the parent D_{6h} benzene-like structure and hexafluoro Dewar benzene.³ The other possible isomers are unknown although they are potential products in these experiments. Nonetheless, a substantial majority of the new bands could be assigned to known species. As listed in Table 1 for experiments without added dopant, the products include: hexafluoro Dewar benzene,

Table 2 Band Positions (cm^{-1}) and Assignments for the Products of the Excimer-Laser Irradiation of C_6F_6 Doped with CCl_4 in Argon Matrices

Band	Ar/ C_6F_6 / CCl_4 =		Ar/ C_6F_6 / CCl_4 =		Assignment
	250/1/1	lamp	250/1/2	lamp	
1772	0.074	...	0.121	...	1,4-cyclo- C_6F_8
1747	0.305	...	0.989	...	1,3- $\text{C}_6\text{F}_5\text{Cl}$ /cyclo- C_6F_8
1736	0.139	...	sh	...	1,4-cyclo- C_6F_8
1728	0.489	...	1.095	...	$\text{C}_6\text{F}_5\text{H}$
1715	0.047	...	0.087	...	1,3-cyclo- C_6F_8
1707	0.168	..	0.489	...	1,3-cyclo- C_6F_8
1700	0.163	...	0.271	...	
1698	0.166	...	0.266	...	
1660	0.084	...	0.150	...	
1652	0.121	...	$\text{C}_6\text{F}_5\text{Cl}$
1598 ^a	0.532	...	0.726	...	
1592 ^c	0.339	0.189	0.721	0.616	H_2O
1512	sh	sh	b	...	$\text{C}_6\text{F}_5\text{Cl}/\text{C}_6\text{F}_5\text{H}$
1501	0.079	...	0.147	...	$\text{C}_6\text{F}_5\text{CH}_3$
1494 ^a	0.266	...	0.668	...	m- $\text{C}_6\text{F}_4\text{Cl}_2$
1484 ^a	0.392	...	0.595	...	o- $\text{C}_6\text{F}_4\text{Cl}_2$
1473 ^a	0.532	0.316	1.047	0.784	C_6F_6^+
1462 ^a	0.400	...	0.508	...	m- $\text{C}_6\text{F}_4\text{Cl}_2$
1440 ^a	0.711	...	0.755	...	$\text{C}_6\text{F}_5\text{Cl}$
1409	0.605	...	1.453	...	$\text{C}_6\text{F}_5\text{H}/\text{m-}\text{C}_6\text{F}_4\text{Cl}_2$
1369 ^a	0.292	...	0.263	...	C_2F_2
1341	0.213	0.176	sh	sh	$\text{C}_6\text{F}_{10} + \text{C}_2\text{F}_4$
1337	0.284	0.166	0.692	0.537	
1331	0.218	...	c	c	$\text{C}_6\text{F}_{10} + \text{C}_2\text{F}_4$
1319	0.911	...	1.642	...	p- $\text{C}_6\text{F}_4\text{Cl}_2$ $\text{C}_6\text{F}_{10} + \text{C}_2\text{F}_4$
1276	0.053	0.034	0.079	0.034	CF/CF ₄
1265	0.066	...	0.087	...	CF ₄
1251	0.139	0.124	c	c	CF ₃
1242	0.155	0.121	0.268	0.211	C_2F_6
1227	0.184	...	0.584	...	$\text{F}_3\text{C}(\text{CC})_2\text{CF}_3$
1225	0.158	...	c, sh	c, sh	CCl_3CF_3
1194	0.089	...	0.203	...	$\text{F}_3\text{C}(\text{CC})_2\text{CF}_3/\text{C}_2\text{F}_4$
1160	0.132	...	sh	sh	$\text{C}_6\text{F}_5\text{Cl}$
1155	0.132	...	0.350	...	C_2F_2
1115	0.011	...	0.050	...	C_2F_6
1095	0.205	...	0.661	0.711	m- $\text{C}_6\text{F}_4\text{Cl}_2$
1075	0.189	...	0.497	0.553	$\text{C}_6\text{F}_5\text{H}/\text{CCl}_3\text{F}$
1068	0.084	...	c	...	$\text{F}(\text{CC})_2\text{F}$
1056	0.032	...	0.016	...	$\text{C}_6\text{F}_5\text{H}$
982	sh	...	c	c	$\text{C}_6\text{F}_5\text{H}$
975	0.197	0.105	c	c	
970	sh	sh	sh	sh	
964	0.334	0.297	0.997	...	$\text{C}_6\text{F}_5\text{H}$
951	0.518	0.482	1.479	...	$\text{C}_6\text{F}_5\text{H}$
938	0.042	0.037	0.221	0.126	$\text{C}_6\text{F}_5\text{CH}_3$
929	0.063	0.021	0.095	0.047	CCl_2^+ (or CCl_4^+)

Table 2 Cont'd

Band	Ar/C ₆ F ₆ /CCl ₄ =		Ar/C ₆ F ₆ /CCl ₄ =		Assignment
	250/1/1	lamp	250/1/2	lamp	
900	0.226	0.100	0.568	0.437	CCl ₃
895	0.221	0.100	0.500	0.400	CCl ₃ /o-C ₆ F ₄ Cl ₂
884	0.079	...	0.126	...	C ₆ F ₂ Cl
872	0.174	...	0.337	0.358	C ₆ F ₃ Cl
866	0.192	...	0.574	0.616	C ₆ F ₃ Cl
849	1.305	...	2.300	...	CCl ₃ F/o-C ₆ F ₄ Cl ₂
841	sh	...	c	c	p-C ₆ F ₄ Cl ₂
821	0.511	...	1.558	...	m-C ₆ F ₄ Cl ₂
712	0.111	0.118	C ₂ F ₆
707	0.105	0.118	C ₂ F ₆
682	0.353	0.389	C ₂ Cl ₆
651	0.126	...	0.358	...	C ₂ F ₂
642	0.050	...	0.158	...	o-, m-C ₆ F ₄ Cl ₂
570	0.132	...	CCl ₃ CF ₃
535	0.095	...	CCl ₃ F
502	0.163	0.047	Cl ₂ ⁺
479	0.074	0.053	
460	0.058	...	
443	0.084	...	CCl ₃ CF ₃
430	0.084	...	CCl ₃ CF ₃

... No change occurred after irradiation with mercury arc lamp.

^a Present in blank experiments but increased in intensity when sample was irradiation during deposition.

^b Overlapped by parent band.

^c Overlapped by product band.

decafluorobiphenyl,^{12,13} octafluorocyclohexadiene (1, 3 and 1, 4 isomers),^{14,15} octafluorotoluene¹⁶ and decafluorocyclohexene.¹⁷ Weaker bands can be assigned to fragmentation products¹⁸⁻²¹ C₂F₄, C₄F₂ and CF₃CCF. Interestingly, in those experiments where CH₄ was an impurity in the system, product absorptions due to C₆F₅H and C₆F₆CH₃ were observed.^{22,23} Several additional bands remain. Two of these, at 1599 and 1677 cm⁻¹, fall very near vibrational modes of the hexakis(trifluoromethyl) derivative of benzvalene,²⁴ and are tentative assigned to hexafluorobenzvalene. Of the remaining bands, most are weak (less than 0.10 absorbance units) and are not readily assigned. They may be due either to absorptions of the other isomers of C₆F₆, or to additional minor products. In any event, it is clear that extensive reaction and product formation occurs following 193 nm irradiation of these samples.

Doping with an electron trap (here, either Cl₂ or CCl₄) is commonly done in matrix photochemistry experiments to enhance photoionization reactions and cation formation. These products are often detected by photobleaching experiments, where Hg arc irradiation releases electrons from the trap, and neutralization of the cation occurs. Of course, the electron trap may enter into the reaction chemistry; both effects were observed here.

Table 2 lists the products observed following 193 nm laser irradiation of Ar/C₆F₆/CCl₄ samples with varying concentration ratios. Many of the products

Table 3 Band Positions (cm⁻¹) and Assignments for the Products of the Excimer-Laser Irradiation of C₆F₆ Doped with Cl₂ in Argon Matrices

<i>Band</i>	<i>Ar/C₆F₆/Cl₂ =</i>		<i>Assignment</i>
	<i>250/1/1</i>	<i>lamp</i>	
3040	0.113	0.150	CH ₃ Cl/CHClF ₂
3025	0.700	0.842	CH ₄
3017	0.568	0.679	CH ₃ F
3015	0.579	0.737	CH ₃ F
2966	0.340	0.000	CH ₃ . . F
2964	0.366	0.461	CH ₃ F
2867	0.053	0.063	CH ₂ Cl
2863	0.074	0.089	CH ₃ F
1772	0.129	0.170	1,4-cyclo-C ₆ F ₈
1746	0.505	0.726	1,3-C ₆ F ₅ Cl/cyclo-C ₆ F ₈
1734	0.718	0.968	1,4-cyclo-C ₆ F ₈
1720	0.216	0.263	C ₆ F ₅ H
1699	0.347	0.516	
1697	0.374	0.482	
1695	0.353	0.526	
1597	0.500	0.405	
1592	0.526	0.000	H ₂ O
1512	0.500	0.495	C ₆ F ₅ Cl/C ₆ F ₅ H
1473 ^a	0.789	0.495	C ₆ F ₆ ⁺
1441	0.826	0.811	C ₆ F ₅ Cl
1405	0.779	1.240	C ₆ F ₅ H
1394	0.237	0.174	
1387	0.189	0.189	
1380	0.232	0.289	C ₆ F ₅ Cl
1347	0.389	0.405	C ₆ F ₅ Cl/CH ₃ Cl
1336	0.779	1.029	C ₆ F ₁₀ + C ₂ F ₄
1315	0.903	1.290	p-C ₆ F ₄ Cl ₂ /C ₆ F ₁₀ + C ₂ F ₄ /CHClF ₂
1276	0.084	0.000	CF
1266	0.126	0.079	CF ₄
1251	sh	0.000	CF ₃
1242	0.268	0.300	C ₂ F ₆ /CHClF ₂
1234	0.205	0.324	F ₃ C(CC) ₂ CF ₃
1220	0.092	0.104	F ₃ C(CC) ₂ CF ₃
1215	0.076	0.089	CF ₃ Cl
1190	0.195	0.254	C ₂ F ₄
1160	0.218	0.326	C ₆ F ₅ Cl
1100	0.179	0.242	C ₆ F ₅ Cl/CF ₃ CCF
1092	0.134	0.135	m-C ₆ F ₄ Cl ₂
1087	0.118	0.112	CHCl ₂ F
1068	0.232	0.312	F(CC) ₂ F
974	0.458	0.000	
971	0.463	0.289	
966	b	0.289	C ₆ F ₅ H
951	b	0.176	C ₆ F ₅ H
897	0.142	0.195	o-C ₆ F ₄ Cl ₂ /F ₂
883	0.182	0.194	C ₆ F ₅ Cl
874	0.495	0.737	C ₆ F ₅ Cl

Table 3 Cont'd

Band	Ar/C ₆ F ₆ /Cl ₂ =		Assignment
	250/1/1	lamp	
864	0.563	0.779	C ₆ F ₅ Cl
847	0.774	1.256	o-C ₆ F ₄ Cl ₂
840	0.379	0.496	p-C ₆ F ₄ Cl ₂
829	0.784	1.155	m-C ₆ F ₄ Cl ₂
819	0.247	0.262	CHCl ₂ F
795	0.200	0.200	CF ₃ Cl
792	0.218	0.054	CF ₃ Cl
781	0.221	0.221	CF ₃ Cl
776	0.205	0.103	CF ₃ Cl
768	0.189	0.189	FCI
746	0.253	0.253	CHCl ₂ F
721	0.274	0.248	
718	0.326	0.417	CH ₃ Cl
716	0.421	0.485	C ₆ F ₅ Cl
713	0.484	0.485	m-C ₆ F ₄ Cl ₂
708	0.325	0.387	C ₂ F ₆
705	...	0.295	C ₂ F ₆
700	...	0.166	
566	0.045	0.068	CF ₃ Cl
479	0.062	0.042	
435	0.051	0.084	(HF) _n

^a Presents in blank experiments but increased in intensity when sample was irradiated during deposition.

^b Overlapped by product band.

observed without added dopant were observed in these experiments as well, although with generally lower yield. In addition, a number of chlorinated products were observed, primarily including C₆F₅Cl and C₆F₄Cl₂ (ortho, meta and para isomers).^{22,25} The CCl₃ radical was seen at 898 cm⁻¹, as has been noted in a previous excimer laser irradiation study²⁶ of CCl₄ and elsewhere,²⁷ along with CCl₃F.^{10,28} Lesser products derived from this pair of reactants are listed in Table 2. It is noteworthy that several product bands were sensitive to Hg arc irradiation; these will be discussed below.

Experiments involving laser irradiation of Ar/C₆F₆/Cl₂ samples led to product formation as well. Many of the products formed were seen in the above experiments, either during the irradiation of Ar/C₆F₆ or Ar/C₆F₆/CCl₄ samples. These are listed in Table 3. Due to CH₄ impurity, additional product containing C, H, F and Cl were observed, as listed in the Table. Additional, new products were also seen, and are assigned in Table 3. Finally, several product absorptions were decreased or destroyed by Hg arc irradiation. Some of these were also seen in the CCl₄-doped experiments, while others were not.

Bands that were destroyed by Hg arc irradiation must be assigned to particularly reactive intermediates, often radical cations when an electron trap is present. Previous studies of the excimer laser irradiation of Ar/CCl₄ samples observed several such

bands, which were assigned in accordance with earlier work to species such as CCl_4^+ and Cl_3^+ , as well as the CCl_3 radical.^{26,27} These bands also observed in this study, and are assigned in Table 2. Additional photosensitive bands common to experiments with both dopants were noted at 479, 1276, 1473 and 1592 cm^{-1} . The first two were quite weak before and after Hg arc irradiation and limited conclusions can be reached about the species responsible for these two absorptions. The latter two were quite intense before irradiation, and showed dramatic reduction upon photobleaching with the Hg arc. While interesting, the limited data preclude definitive assignment to the absorbing species. Nonetheless, realistic possibilities should be discussed.

The most likely cationic product in this system is the parent radical cation, C_6F_6^+ , a species seen by emission spectroscopy after 193 nm excimer laser irradiation^{29,30} of gaseous and argon matrix samples containing C_6F_6 . The selection rules for emission spectra, however, lead to observation of the totally symmetric modes of the emitting species, while infrared spectra show the antisymmetric modes. Thus, bands observed in emission are not anticipated in the infrared spectrum. However, a salt containing the C_6F_6^+ cation has been prepared³¹ (with the AsF_6^- anion). The infrared spectrum of this salt shows a strong absorption at 1490 cm^{-1} , close to the 1473 cm^{-1} band observed here. Antisymmetric C—F stretching modes of aromatic fluorides are anticipated in this region, so assignment of the 1473 cm^{-1} band seen here to C_6F_6^+ is likely. The first ionization threshold⁶ for C_6F_6 is around 10 eV which is readily accessible by absorption of two photons. Multiphoton ionization of CCl_4 has been seen under identical conditions,²⁶ so that formation of C_6F_6^+ (and presumably Cl^-) is quite reasonable. CCl_4 serves as an effective electron trap by dissociative attachment, leading to CCl_3 cage-paired with Cl^- . Hg irradiation may lead to electron detachment, neutralization of cations, and reduction in bands due to the CCl_3 radical. This reduction was also observed, with the band near 900 cm^{-1} due to the CCl_3 radical decreasing significantly upon irradiation.

While assignment of the 1592 cm^{-1} band to another mode of the C_6F_6^+ cation is possible, the salt spectrum showed no additional intense bands in this region. Another, more likely, assignment is to non-rotating H_2O in the argon matrix. Many researchers have noted that, in general, H_2O rotates in solid argon, and gives rise to a well known spectrum.³² However, when certain impurities, including cations, are introduced into the matrix, this rotation is quenched and “non-rotating” H_2O is detected³³ near 1592 cm^{-1} . It has been observed³⁴ that when cations in the matrix are photobleached, the local electric field is reduced and the H_2O molecules are able to rotate. The band at 1592 cm^{-1} is reduced, and the normal spectrum of “rotating” H_2O is seen. While not definitive, this provides a reasonable explanation for this band, one that is in agreement with previous studies.

A few weak, photosensitive bands remain, at 1337 cm^{-1} in the CCl_4 doped experiments and at $971,974\text{ cm}^{-1}$ in the Cl_2 doped experiments. The $971,974\text{ cm}^{-1}$ doublet was on the low energy shoulder of a very intense band of parent C_6F_6 which made reproducible observation of this band difficult. It may also have been in the CCl_4 experiments, but hidden by the parent band. This position is close and slightly to the red of an intense band at 1020 cm^{-1} for the C_6F_6^+ cation in salts. Given the dif-

difficulty in reproducibly detecting this doublet, such an assignment must be viewed as very tentative. The 1337 cm^{-1} band was in a very congested spectral region, and consequently might have escaped detection in the Cl_2 experiments. This band was relatively weak, and thus any assignment would be very speculative.

Comparison with Previous Studies

Infrared multiphoton photochemistry of C_6F_6 in the gas phase reported C_2F_4 as the major product.³⁵ These researchers propose initial formation of $\text{C}_6\text{F}_5\cdot + \text{F}$, followed by a sequence of steps leading to the observed product. Bryce-Smith and coworkers³⁶ argue, at least in solution, C—F bond breakage is not the initial step due to the very strong C—F bond, and that the solvent plays a significant role in the process. Earlier corona discharge studies³⁷ of C_6F_6 samples followed by matrix trapping led to isolation of a significant yield of decafluorobiphenyl, $\text{C}_{12}\text{F}_{10}$, which was taken as indication of the initial formation of C_6F_5 . $\text{C}_{12}\text{F}_{10}$ was very weakly observed at best in the present experiments despite the fact that the infrared spectrum is well known. This argues that in the present study C—F bond to rupture to form the C_6F_5 radical is not a major process.

Haller³ has studied this system extensively, and suggested three competing isomerization processes for C_6F_6 from higher singlet states. Path (a) involves isomerization to hexafluoro-Dewar benzene from the E_{2g} (S_3) or B_{1u} (S_2) state of C_6F_6 . Path (b) produces the hexafluorobicyclo (3.1.0) hexenylene biradical from any of the three singlet states S_1 , S_2 or S_3 , with little or no activation energy. It is important to note that this biradical is not involved in formation of the Dewar isomer, and is proposed to revert back to C_6F_6 . As such, it is the major competition for isomerization to the Dewar isomer. Path (c) produces hexafluorobenzvalene from the B_{1u} (S_2) state with no activation energy required and from B_{2u} (S_1) with an activation energy required.

This mechanism fits many of the observations here, particularly that hexafluoro-Dewar benzene was a major product in these studies, in agreement with path (a). In addition, two bands were observed where hexafluorobenzvalene is anticipated to absorb, as predicted by path (c). Of course, path (b) leads to reformation of the parent species, and would not be directly observable. With the photon flux employed here, additional photochemistry may occur, either from absorption of a photon by the initial products or absorption of a second photon by excited C_6F_6 . This would lead to the more extensive fragmentation that was also observed. Finally, CH_4 was an impurity in the present experiments, and products such as $\text{C}_6\text{F}_5\text{H}$ and $\text{C}_6\text{F}_5\text{CH}_3$ were detected. This agrees well with a previous study²³ where C_6F_6 and CH_4 were intentionally mixed and irradiated, and the same products ($\text{C}_6\text{F}_5\text{H}$ and $\text{C}_6\text{F}_5\text{CH}_3$) were seen.

In the experiments doped with either CCl_4 or Cl_2 , additional chlorine-containing products were observed. These included $\text{C}_6\text{F}_5\text{Cl}$, and o-, m-, and p- $\text{C}_6\text{F}_4\text{Cl}_2$. Since the C—Cl bond is readily ruptured by a 193 nm photon, and since extensive fragmentation and rearrangement occurs in the absence of the dopant, it is not surprising that chlorine incorporation into the product species occurs. It is possible that a

specific complex between C_6F_6 and either Cl_2 or CCl_4 is formed prior to the photochemical event, but the evidence for this is only indirect.

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