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

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193 nm excimer laser irradiation of Ar/C_6F_6 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 Cl_2 or CCl_4 was doped into the Ar/C_6F_6 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 $C_6F_6^+$ cation. A comparison to previous studies of the photochemistry of C_6F_6 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 C_6F_6 are well known, much less is known about the isomeric forms of C_6F_6. Only hexafluoro Dewar benzene has been reported,[3] while very little is known about the hexafluorobenzvalene, prismane or fulvene isomers. In addition, while C_6F_6 has been the object of several photochemical studies,[3,4] these have not been at 193 nm, where C_6F_6 is known to absorb strongly.[5] Also, while the gas phase photochemistry of C_6F_6 has been examined, matrix trapping of intermediates has not been attempted to date.

Finally, the photoelectron transitions for hexafluorobenzene occur[6] 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/C_6F_6 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 C_6F_6 (Aldrich) were deposited onto a CsI cold window maintained at 14 K. Some samples were doped with either Cl_2 (Matheson) or CCl_4 (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, CH_4 was observed as a minor impurity arising from the walls of the vacuum system.

Several initial experiments were carried out irradiating Ar/C_6F_6 and $Ar/C_6F_6/Cl_2$ 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/C_6F_6 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$_6$F$_6$ in Argon Matrices

| Band | Ar/C$_6$F$_6$ = | | Assignment |
	500/1	1000/1	
1772	0.079	0.047	1,4-cyclo-C$_6$F$_8$
1751	0.759	0.296	Hexafluoro Dewar-benzene
1740	0.034	0.024	1,3-cyclo-C$_6$F$_8$
1733	0.028	0.026	1,4-cyclo-C$_6$F$_8$
1722	0.294	0.093	C$_6$F$_5$H
1717	sh	0.054	1,3-cyclo-C$_6$F$_8$
1715	sh	0.051	1,3-cyclo-C$_6$F$_8$
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	C$_6$F$_5$H
1512	0.368	0.118	C$_6$F$_5$H
1501	0.326	0.111	C$_6$F$_5$CH$_3$/C$_{12}$F$_{10}$
1428	0.403	0.147	C$_6$F$_5$CF$_3$
1424	0.465	0.169	C$_6$F$_5$CF$_3$
1411	0.323	0.110	C$_6$F$_5$H
1358[a]	0.661	0.447	C$_6$F$_5$CF$_3$
1341	0.142	0.077	Hexafluoro Dewar-benzene
1327	0.103	0.030	C$_2$F$_4$
1311	0.195	0.092	C$_6$F$_{10}$
1268	0.051	0.019	Hexafluoro Dewar-benzene
1230	0.068	0.010	Hexafluoro Dewar-benzene
1184	0.099	0.032	C$_2$F$_4$
1132	0.063	0.013	C$_6$F$_5$CH$_3$
1103	0.068	0.021	CF$_3$CCF
1080	0.126	0.025	Hexafluoro Dewar-benzene/C$_{12}$F$_{10}$
1074	0.101	0.030	C$_6$F$_5$H
1065	0.136	0.023	F(CC)$_2$F
1057	0.189	0.053	C$_6$F$_5$H
1010	sh	sh	C$_6$F$_5$CF$_3$
994	sh	sh	C$_6$F$_{10}$
990	sh	sh	C$_2$F$_4$
986	sh	sh	C$_{12}$F$_{10}$
980	0.142	0.048	C$_6$F$_5$H
972	0.191	0.047	C$_6$F$_5$H
963	0.037	0.026	C$_6$F$_5$H
958	0.032	. . .	C$_6$F$_5$CH$_3$
953	0.042	0.021	C$_6$F$_5$H
947	0.026	0.021	
938	0.021	0.008	C$_6$F$_5$CH$_3$
926	0.656	0.254	Hexafluoro Dewar-benzene
884	0.050	0.032	Hexafluoro Dewar-benzene
675	. . .	0.093	

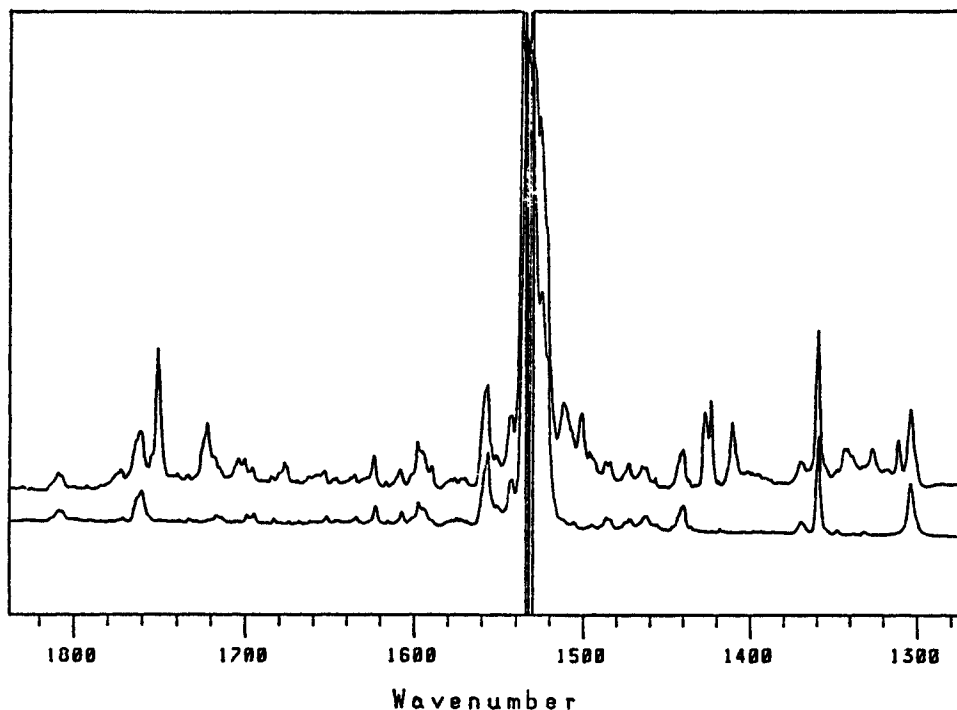[a]Present at lower intensity in experiments without irradiation.
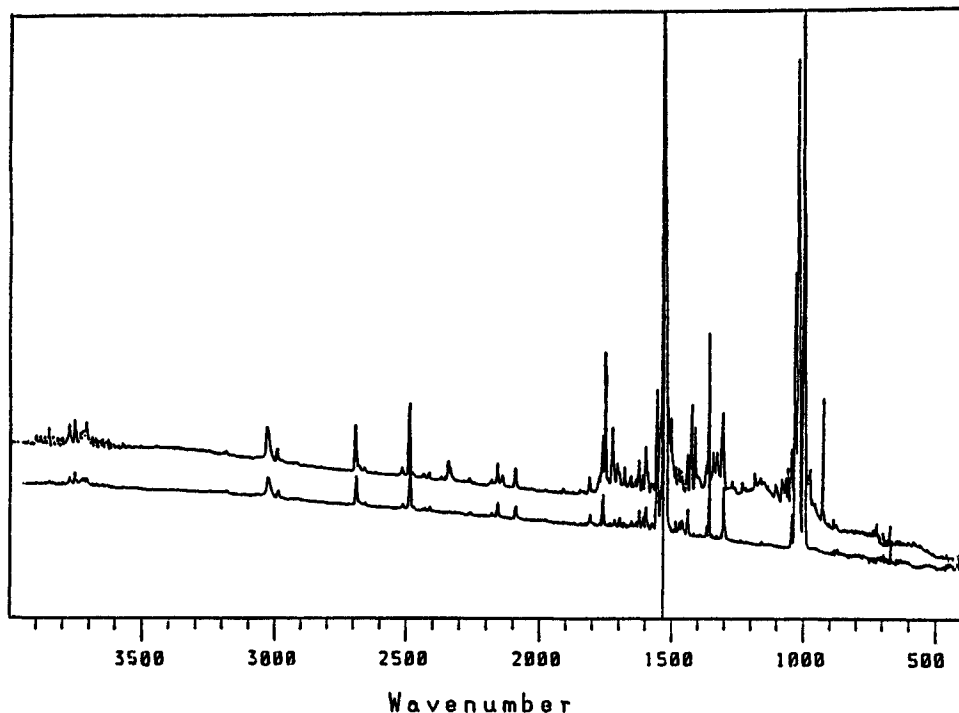
Figure 1   Infrared spectra, from 400 to 4000 cm^{-1}, of a sample of Ar/C$_6$F$_6$ = 500 subjected to 193 nm excimer laser irradiation during deposition (upper trace) compared.to a spectrum of a similar sample without irradiation (lower trace).

In a second set of experiments, samples of Ar/C$_6$F$_6$/CCl$_4$ were irradiated during deposition, at several different concentration ratios. In these experiments, many new product absorptions were noted, an listed in Table 2. A number of these coincide with product absorptions observed above when C$_6$F$_6$ 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 Ar/C$_6$F$_6$/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 Ar/C$_6$F$_6$/CCl$_4$ experiments. All of the product bands in the Ar/C$_6$F$_6$/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 Ar/C$_6$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 studies[2] 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$_6$F$_6$ 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-C_6F_5Cl/cyclo-C_6F_8
1736	0.139	...	sh	...	1,4-cyclo-C_6F_8
1728	0.489	...	1.095	...	C_6F_5H
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	...	C_6F_5Cl
1598[a]	0.532	...	0.726	...	
1592[c]	0.339	0.189	0.721	0.616	H_2O
1512	sh	sh	b	...	C_6F_5Cl/C_6F_5H
1501	0.079	...	0.147	...	$C_6F_5CH_3$
1494[a]	0.266	...	0.668	...	m-$C_6F_4Cl_2$
1484[a]	0.392	...	0.595	...	o-$C_6F_4Cl_2$
1473[a]	0.532	0.316	1.047	0.784	$C_6F_6^+$
1462[a]	0.400	...	0.508	...	m-$C_6F_4Cl_2$
1440[a]	0.711	...	0.755	...	C_6F_5Cl
1409	0.605	...	1.453	...	C_6F_5H/m-$C_6F_4Cl_2$
1369[a]	0.292	...	0.263	...	C_2F_2
1341	0.213	0.176	sh	sh	C_6F_{10} + C_2F_4
1337	0.284	0.166	0.692	0.537	
1331	0.218	...	c	c	C_6F_{10} + C_2F_4
1319	0.911	...	1.642	...	p-$C_6F_4Cl_2$
					C_6F_{10} + C_2F_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	...	$F_3C(CC)_2CF_3$
1225	0.158	...	c, sh	c, sh	CCl_3CF_3
1194	0.089	...	0.203	...	$F_3C(CC)_2CF_3$/C_2F_4
1160	0.132	...	sh	sh	C_6F_5Cl
1155	0.132	...	0.350	...	C_2F_2
1115	0.011	...	0.050	...	C_2F_6
1095	0.205	...	0.661	0.711	m-$C_6F_4Cl_2$
1075	0.189	...	0.497	0.553	C_6F_5H/CCl_3F
1068	0.084	...	c	...	$F(CC)_2F$
1056	0.032	...	0.016	...	C_6F_5H
982	sh	...	c	c	C_6F_5H
975	0.197	0.105	c	c	
970	sh	sh	sh	sh	
964	0.334	0.297	0.997	...	C_6F_5H
951	0.518	0.482	1.479	...	C_6F_5H
938	0.042	0.037	0.221	0.126	$C_6F_5CH_3$
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$_5$Cl
872	0.174	...	0.337	0.358	C$_6$F$_5$Cl
866	0.192	...	0.574	0.616	C$_6$F$_5$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] octa-fluorotoluene[16] and decafluorocyclohexene.[17] Weaker bands can be assigned to fragmentation products[18-21] C$_2$F$_4$, C$_4$F$_2$ and CF$_3$CCF. Interestingly, in those experiments where CH$_4$ was an impurity in the system, product absorptions due to C$_6$F$_5$H and C$_6$F$_6$CH$_3$ 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 C$_6$F$_6$, 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 Cl$_2$ or CCl$_4$) 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/C$_6$F$_6$/CCl$_4$ 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 C_6F_6 Doped with Cl_2 in Argon Matrices

| Band | Ar/C_6F_6/Cl_2 = | | Assignment |
	250/1/1	lamp	
3040	0.113	0.150	CH_3Cl/$CHClF_2$
3025	0.700	0.842	CH_4
3017	0.568	0.679	CH_3F
3015	0.579	0.737	CH_3F
2966	0.340	0.000	CH_3...F
2964	0.366	0.461	CH_3F
2867	0.053	0.063	CH_3Cl
2863	0.074	0.089	CH_3F
1772	0.129	0.170	1,4-cyclo-C_6F_8
1746	0.505	0.726	1,3-C_6F_5Cl/cyclo-C_6F_8
1734	0.718	0.968	1,4-cyclo-C_6F_8
1720	0.216	0.263	C_6F_5H
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_2O
1512	0.500	0.495	C_6F_5Cl/C_6F_5H
1473[a]	0.789	0.495	$C_6F_6^+$
1441	0.826	0.811	C_6F_5Cl
1405	0.779	1.240	C_6F_5H
1394	0.237	0.174	
1387	0.189	0.189	
1380	0.232	0.289	C_6F_5Cl
1347	0.389	0.405	C_6F_5Cl/CH_3Cl
1336	0.779	1.029	C_6F_{10} + C_2F_4
1315	0.903	1.290	p-$C_6F_4Cl_2$/C_6F_{10} + C_2F_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_2F_6/$CHClF_2$
1234	0.205	0.324	$F_3C(CC)_2CF_3$
1220	0.092	0.104	$F_3C(CC)_2CF_3$
1215	0.076	0.089	CF_3Cl
1190	0.195	0.254	C_2F_4
1160	0.218	0.326	C_6F_5Cl
1100	0.179	0.242	C_6F_5Cl/CF_3CCF
1092	0.134	0.135	m-$C_6F_4Cl_2$
1087	0.118	0.112	$CHCl_2F$
1068	0.232	0.312	$F(CC)_2F$
974	0.458	0.000	
971	0.463	0.289	
966	b	0.289	C_6F_5H
951	b	0.176	C_6F_5H
897	0.142	0.195	o-$C_6F_4Cl_2$/F_2
883	0.182	0.194	C_6F_5Cl
874	0.495	0.737	C_6F_5Cl

Table 3 Cont'd

| Band | Ar/C_6F_6/Cl_2 = | | Assignment |
	250/1/1	lamp	
864	0.563	0.779	C_6F_5Cl
847	0.774	1.256	o-$C_6F_4Cl_2$
840	0.379	0.496	p-$C_6F_4Cl_2$
829	0.784	1.155	m-$C_6F_4Cl_2$
819	0.247	0.262	$CHCl_2F$
795	0.200	0.200	CF_3Cl
792	0.218	0.054	CF_3Cl
781	0.221	0.221	CF_3Cl
776	0.205	0.103	CF_3Cl
768	0.189	0.189	FCl
746	0.253	0.253	$CHCl_2F$
721	0.274	0.248	
718	0.326	0.417	CH_3Cl
716	0.421	0.485	C_6F_5Cl
713	0.484	0.485	m-$C_6F_4Cl_2$
708	0.325	0.387	C_2F_6
705	...	0.295	C_2F_6
700	...	0.166	
566	0.045	0.068	CF_3Cl
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 C_6F_5Cl and $C_6F_4Cl_2$ (ortho, meta and para isomers).[22,25] The CCl_3 radical was seen at 898 cm^{-1}, as has been noted in a previous excimer laser irradiation study[26] of CCl_4 and elsewhere,[27] along with CCl_3F.[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/C_6F_6/Cl_2 samples led to product formation as well. Many of the products formed were seen in the above experiments, either during the irradiation of Ar/C_6F_6 or Ar/C_6F_6/CCl_4 samples. These are listed in Table 3. Due to CH_4 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 CCl_4-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/CCl_4 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 prepared[31] (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 threshold[6] 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 detected[33] near 1592 cm^{-1}. It has been observed[34] 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 cm^{-1} in the Cl_2 doped experiments. The 971,974 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-

ficulty in reproducibly detecting this doublet, such an assignment must be viewed an very tentative. The 1337 cm^{-1} 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$_6$F$_6$ in the gas phase reported C$_2$F$_4$ as the major product.[35] These researchers propose initial formation of C$_6$F$_5$• + F, followed by a sequence of steps leading to the observed product. Bryce-Smith and coworkers[36] 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 studies[37] of C$_6$F$_6$ samples followed by matrix trapping led to isolation of a significant yield of decafluorobiphenyl, C$_{12}$F$_{10}$, which was taken as indication of the initial formation of C$_6$F$_5$. C$_{12}$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$_6$F$_5$ radical is not a major process.

Haller[3] has studied this system extensively, and suggested three competing isomerization processes for C$_6$F$_6$ 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$_6$F$_6$. 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$_6$F$_6$. 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$_6$F$_6$. 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 C$_6$F$_5$H and C$_6$F$_5$CH$_3$ were detected. This agrees well with a previous study[23] where C$_6$F$_6$ and CH$_4$ were intentionally mixed and irradiated, and the same products (C$_6$F$_5$H and C$_6$F$_5$CH$_3$) were seen.

In the experiments doped with either CCl$_4$ or Cl$_2$, additional chlorine-containing products were observed. These included C$_6$F$_5$Cl, and o-, m-, and p-C$_6$F$_4$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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