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Multiphoton Ionization of Chloromethanes with 193-nm Excimer Laser Radiation in Argon Matrices

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The 193-nm output of an excimer laser has been coupled with the matrix isolation technique to demonstrate the feasibility of multiphoton ionization of matrix-isolated species. CCl_4, $CHCl_3$, and CH_2Cl_2 were, in turn, deposited in argon and (in some cases) nitrogen matrices and irradiated for between 5 min and 3 h. For CCl_4 and CH_2Cl_2, the major product was the parent cation or species derived directly thereform, while more varied species, including the $CHCl_3^-$ anion, were observed in the $CHCl_3$ studies. In addition, neutral fragments were observed in a manner similar to previous resonance radiation and proton-beam radiolysis studies. Irradiation of the sample mixture during the deposition process led to increased product yield, as well as additional products for some of the systems. The laser irradiation time, power, and repetition rate were varied over a wide range, and a relative insensitivity to these parameters was noted.

Introduction

Chemists have long been interested in the spectroscopy and structure of molecular ions, for comparison to their neutral counterparts. However, in condensed media, the ions of interest are either highly solvated or ion paired such that the bare ion is not actually examined. Recent advances in gas-phase spectroscopy, particularly development of the velocity modulation technique, have allowed high-resolution spectroscopic study of a number of ions.[1-3] These workers are limited to relatively small ions and, to some degree, by the availability of tunable laser sources for spectroscopic studies. Matrix isolation is an extremely powerful technique[4-7] for the study of unstable species, including molecular ions. This approach allows the buildup of a sample with time, increasing the signal strength, and can be followed by examination with conventional spectroscopic techniques. In those cases where ions have been studied in the gas phase and in matrices, only relatively small shifts have been observed.

The formation of ions for matrix isolation studies has long been a limitation to this approach. The two major techniques to date have been vacuum ultraviolet irradiation from windowless discharges and proton-beam bombardment of depositing samples.[5,6,8-22] These two approaches yielded largely the same set of neutrals and ions for a given chemical system. In particular, considerable fragmentation and secondary reaction was observed for most systems, as well as the parent molecular cation. This is, in part, a consequence of the fact that these energy sources must be applied during the deposition process, as neither vacuum UV photons nor high-energy protons are able to penetrate a significant distance into the matrix. As a consequence, the initial photoproducts are formed while still mobile and have the opportunity to react further before being quenched into a stable matrix site. A secondary drawback to these approaches is a relatively low photon or proton flux onto the matrix sample.

The development and improvement of laser technology continues to offer new and exciting possibilities as photochemical light sources. Excimer lasers, operating on the ArF* line at 193 nm, are often used in conjunction with mass spectrometric techniques for multiphoton ionization. Recent studies in this laboratory have coupled excimer laser irradiation with matrix isolation and have demonstrated the feasibility of inducing unimolecular and bimolecular chemical reactions.[23-25] A very recent report presented preliminary evidence for the multiphoton ionization of CCl_4 by 193-nm laser radiation within an argon matrix.[26] The full study of CCl_4 photoionization is presented here, along with the complementary 193-nm matrix photochemistry of $CHCl_3$ and CH_2Cl_2. The photochemistry and photophysics of these chlorocarbons have been the subject of previous studies, including gas-phase photolysis by 193-nm excimer laser irradiation.[27-31] These compounds are also of particular interest in the fields of atmospheric and environmental chemistry.[32]

Experimental Section

The experiments in this study were performed on conventional matrix isolation equipment that has been described previously.[23,26,33-35] Carbon tetrachloride (MCB), chloroform (MCB),

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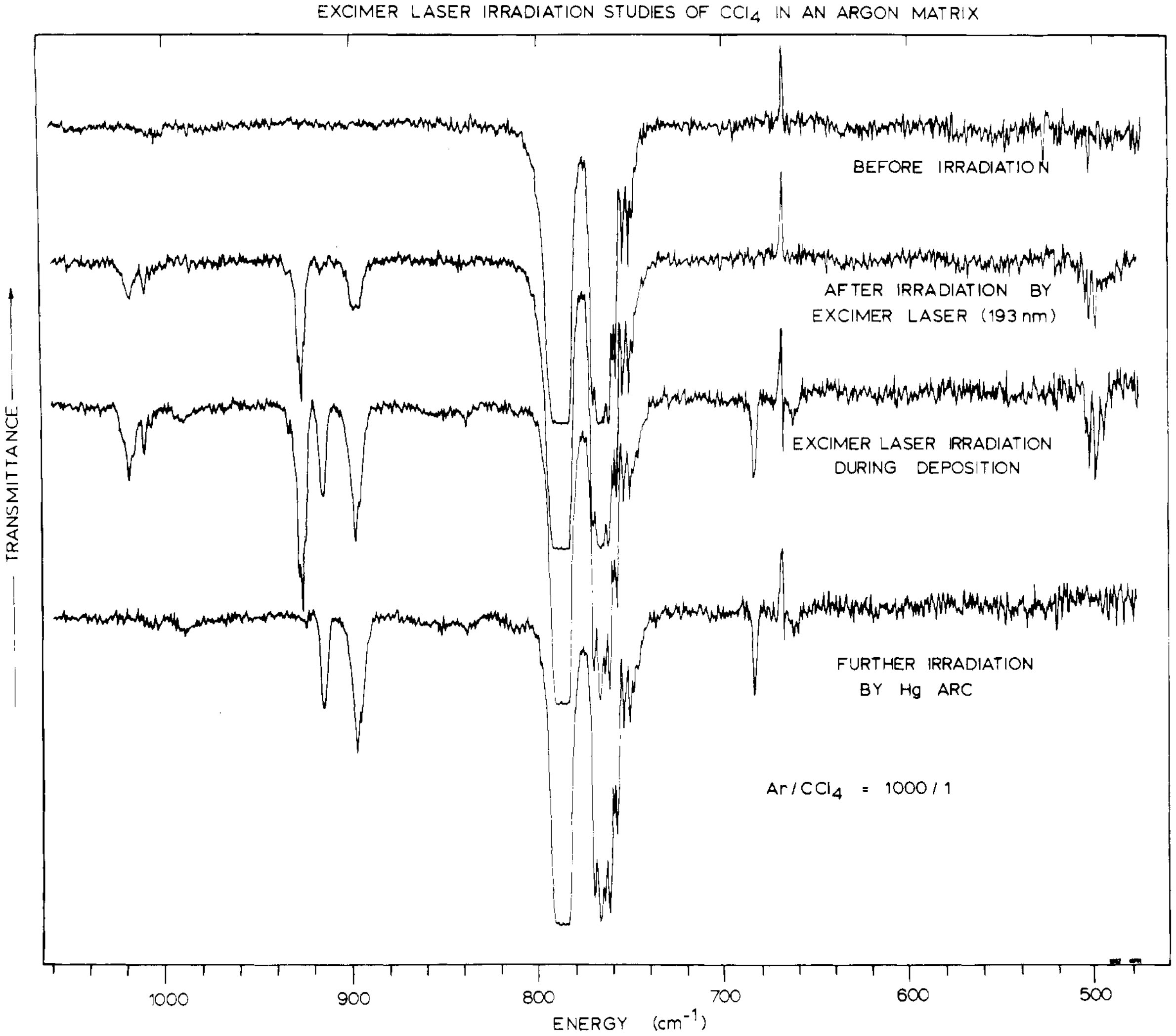

Figure 1. Infrared spectrum of CCl_4 isolated in an argon matrix (top trace), compared to spectra obtained after 193-nm excimer laser irradiation. The second trace shows the products of an in situ 193-nm laser irradiation, while the third trace shows the spectrum obtained after laser irradiation during deposition. The bottom trace shows the results of subsequent irradiation of this sample by a medium-pressure Hg arc.

chloroform-*d* (99.8% d, Aldrich), and methylene chloride (Fisher) were introduced into the vacuum line as the vapor above the liquid, after degassing through repeated freeze–thaw cycles at 77 K. Argon and nitrogen were used as the matrix gases without further purification. Samples with concentration ratios (matrix/reactant, M/R) between 250/1 and 1000/1 were deposited at 1–2 mmol/h on a CsI window held at roughly 14 K. Final spectra were recorded on a Mattson Cygnus FTIR at 1-cm^{-1} resolution from 400 to 4000 cm^{-1}.

Two arrangements were used for excimer laser irradiation of matrix samples. A number of the matrix samples were irradiated with the laser after deposition (in situ), with the matrix rigidly frozen in place. In these experiments, after the final infrared spectrum was obtained, the cold window was rotated and the laser beam entered the cold cell through a suprasil window. After irradiation, the refrigerator was rotated back, and additional infrared spectra were recorded. In the second type of experiment, the deposition and irradiation processes were carried out simultaneously; matrices were deposited for approximately 1 h, after which the cold window was rotated and irradiation carried out as before with continued deposition. After roughly 20 h, the deposition and irradiation were stopped, the window was rotated back perpendicular to the infrared beam, and final IR spectrum was recorded. A Lambda Physik excimer laser, Model EMG 103 MSC, was employed using the ArF* line at 193 nm and a repetition rate between 5 and 15 Hz, leading to an average power near 1 W (typical average powers near 10 W were recorded at 100 Hz). In some in situ experiments, samples were irradiated with the H_2O-filtered output of a medium-pressure Hg arc lamp before laser irradiation, and no significant changes were noted. In other experiments, samples were irradiated with the Hg arc after laser irradiation, and distinct changes were noted, as reported below.

Results

In all of the studies conducted here, the initial spectra of the reactants before irradiation were in good agreement with literature spectra.[36-41] During the laser irradiation process, no pressure or temperature rise was noted. However, a bright blue-green fluorescence was noted, which was initially uniform over the matrix but gradually diminished over the course of the irradiation.

CCl_4 Studies. In an initial experiment, a sample of Ar/CCl_4 was deposited for roughly 20 h and then irradiated by the excimer laser at 193 nm. New absorptions were noted after irradiation, including a weak multiplet with maxima at 498, 501, and 503 cm^{-1}, along wth bands at 898 (w), 915 (vw), 926 (m, with slight splittings), 1011 (w), and 1019 (w) cm^{-1}, as shown in Figure 1.

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This sample was then irradiated with the Hg arc for approximately 1 h with a series of Corning filters, and several of the product bands showed photoactivity. When irradiated with light of wavelength between 510 and 900 nm, the bands at 926, 1011, and 1019 cm^{-1} disappeared, along with the multiplet near 500 cm^{-1}, while the bands at 898 and 915 cm^{-1} were unaffected. When irradiated with light of wavelength 300–500 nm or with the full light of the H_2O-filtered Hg arc, the band at 898 cm^{-1} decreased slightly, while the band at 915 cm^{-1} was unaffected. These results were reproduced in a series of experiments at a variety of concentrations. When a similar experiment was carried out in a nitrogen matrix, analogous results were obtained, with bands at 500 (m), 504 (m), 853 (w, br), 902 (w, with splittings), 933 (m), and 1033 (m) cm^{-1}.

A series of experiments was conducted in which the Ar/CCl_4 sample was irradiated during the deposition process. In a typical experiment (see Figure 1), a roughly 2-fold increase in product yield was noted, with the exception of the band at 915 cm^{-1} that increased very substantially. In addition, one new product absorption was noted, at 683 cm^{-1}. Subsequent irradiation by the filtered Hg arc led to the same photobleaching behavior reported above; the 683-cm^{-1} band was unaffected by Hg arc irradiation. Figure 1 shows the products of excimer laser irradiation of samples of Ar/CCl_4 and subsequent photobleaching activity.

A number of experiments were conducted to evaluate parameters affecting product yield in these experiments, including power dependence. In one experiment, the sample was irradiated in situ for 10 min, spectra were recorded, and then the sample was irradiated for another 30 min. No growth in product absorption was noted after the second irradiation. In a related experiment, the laser power was reduced considerably and irradiation was carried out for 5 min; a comparable product yield to that in the above experiment was observed. Finally, reducing the laser power to 0.05 W (measured at 5 Hz, the repetition rate employed) and irradiating for 5 min produced roughly two-thirds of the final product yield, as measured by continued irradiation and comparison to other experiments. On the other hand, the product yield from a given irradiation was proportional to the amount of sample deposited.

In those experiments where irradiation was carried out during deposition, where all species possess more mobility and the ability to separate, the overall product yield was clearly increased. In this series of experiments, deposition lasted 4 h, and irradiation took place during the last 3 h. The dependence of product yield on repetition rate (between 5 and 15 Hz) and on laser power (between 0.15 and 1.5 W) was investigated in a series of these experiments, and no significant differences in yield or product ratios were found, suggesting that maximum conversion to product was obtained very quickly under the conditions selected.

$CHCl_3$ Studies. Samples of Ar/$CHCl_3$ were studied in a number of in situ irradiation experiments, leading to the observation of a number of product absorptions. In an experiment employing in situ irradiation for 1 h at 5 Hz, product absorptions included multiplets near 650 and 785 cm^{-1}; bands at 995, 1219, 1252, and 1303 cm^{-1}; and a very weak, broad absorption near 2800 cm^{-1}. Continued laser irradiation for 160 min at 10 Hz brought out a slight increase in the 1219-cm^{-1} band and a new feature at 898 cm^{-1}. While several of these overlapped parent absorptions, the bands at 652, 898, and 995 cm^{-1} were baseline-resolved and had absorbances of 0.6, 0.1, and 0.15, respectively. Hg arc irradiation of this sample led to destruction of the bands near 650, 785, 995, 1252, and 1303 cm^{-1}, while the 898- and 1219-cm^{-1} features were unaffected. Laser irradiation experiments during deposition led to similar spectral features with increased intensity, including some new splittings and new weak features at 915 and 3087 cm^{-1}. The product absorptions at 652, 898, and 995 cm^{-1} had absorbances of 0.8, 0.25, and 0.2, respectively. Similar results were obtained after Hg arc irradiation; the new feature at 915 cm^{-1} was observed to grow as a result of this irradiation, while the feature at 3087 cm^{-1} disappeared.

An experiment was carried out to determine the wavelength dependence of Hg arc photobleaching, the results of which are summarized in Table I. Laser irradiation at 193 nm was carried out during deposition, producing the product absorptions reported above. The matrix sample was then sequentially irradiated by the Hg arc with a series of Corning filters with differing short-wavelength cutoffs, starting with the 680-nm cutoff filter; the effect of the irradiation on each of the product bands is noted in Table I. Spectra of the products of 193-nm laser irradiation of matrices containing $CHCl_3$ are shown in Figure 2.

TABLE I: Product Band Positions and Mercury Arc Photolysis Behavior after 193-nm Laser Irradiation of Argon Matrices Containing $CHCl_3$

posn, cm^{-1}	descr (orig)	680 nm, 20 min	600 nm, 20 min	600 nm, 70 min addl	Hg arc, 70 min	label
3087	w	none	decr	gone		A
2800	m, br	none	none	none	none	C
1304	w	none	decr	gone		A
1252	w	none	decr	gone		A
1220	m^a	none	none	none	none	C
995	m	none	decr	decr	decr (w)	B
990	m	none	decr	decr	decr (vw)	B
916	w	none	none	none	incr (m)	D
898	m	none	none	none	none	C
896	sh	none	none	none	none	C
785	m^b	none	decr	decr	decr (w)	B
652	s	none	decr	gone		A
648	vs	none	decr	gone		A
641	w	none	gone			A

^{a}Overlaps parent absorption at 1223 cm^{-1}. ^{b}Center of multiplet with maxima at 781, 783, 785, 788, and 790 cm^{-1}.

TABLE II: Product Band Positions and Mercury Arc Photolysis Behavior after 193-nm Laser Irradiation of Argon Matrices Containing $CDCl_3$

posn, cm^{-1}	descr (orig)	600 nm, 20 min	Hg arc, 90 min	label
2305	w	gone		A
2040	w, br	none	none	C
1060	m	decr	gone	A
1038	w	gone		A
794	m	none	decr	B
754	m^a	decr	gone	A
523	s	decr	gone	A

^{a}Center of multiplet overlapping 740-cm^{-1} parent.

A sample of Ar/$CDCl_3$ was also subjected to in situ excimer laser irradiation, leading to the formation of new absorptions at 523 (m), 752, 754, 758 (w multiplet, slightly overlapping a parent absorption at 740 cm^{-1}), 794 (vw, br), 1038 (vw), 1060 (w,), and 2304 (vw) cm^{-1}. All of these bands were subsequently destroyed by irradiation with the H_2O-filtered output of the Hg arc. A smilar sample was irradiated by the laser during deposition, leading to formation of the above product bands with considerably greater intensity, along with a new weak, broad absorption at 2040 cm^{-1}. Hg arc irradiation again led to the destruction of all of these bands, except the band at 795 cm^{-1}, which decreased significantly but was not destroyed, and the absorption at 2040 cm^{-1}, which was unaffected. Finally, a sample of Ar/$CDCl_3$ was irradiated by the laser during deposition, followed by a wavelength dependence study of the Hg arc irradiation. The results of this experiment are presented in Table II.

One experiment was conducted in which a sample containing equal amounts of $CHCl_3$ and $CDCl_3$ in argon was irradiated at 193 nm during deposition. No new products were noted, other than those reported above for the individual reagents. The subsequent Hg arc irradiation behavior of these bands was the same as before.

CH_2Cl_2 Studies. A sample of Ar/CH_2Cl_2 was codeposited and irradiated after deposition with the excimer laser for 1 h at 5 Hz. Two distinct product absorptions were noted in this experiment: a strong band at 763 cm^{-1} and a weak but reproducible absorption at 1102 cm^{-1}. When the matrix was subsequently irradiated with the Hg arc source for 1 h, the band at 763 cm^{-1} was completely destroyed, while no significant change was noted in the 1102-cm^{-1} band. When a similar sample of Ar/CH_2Cl_2 was irradiated with

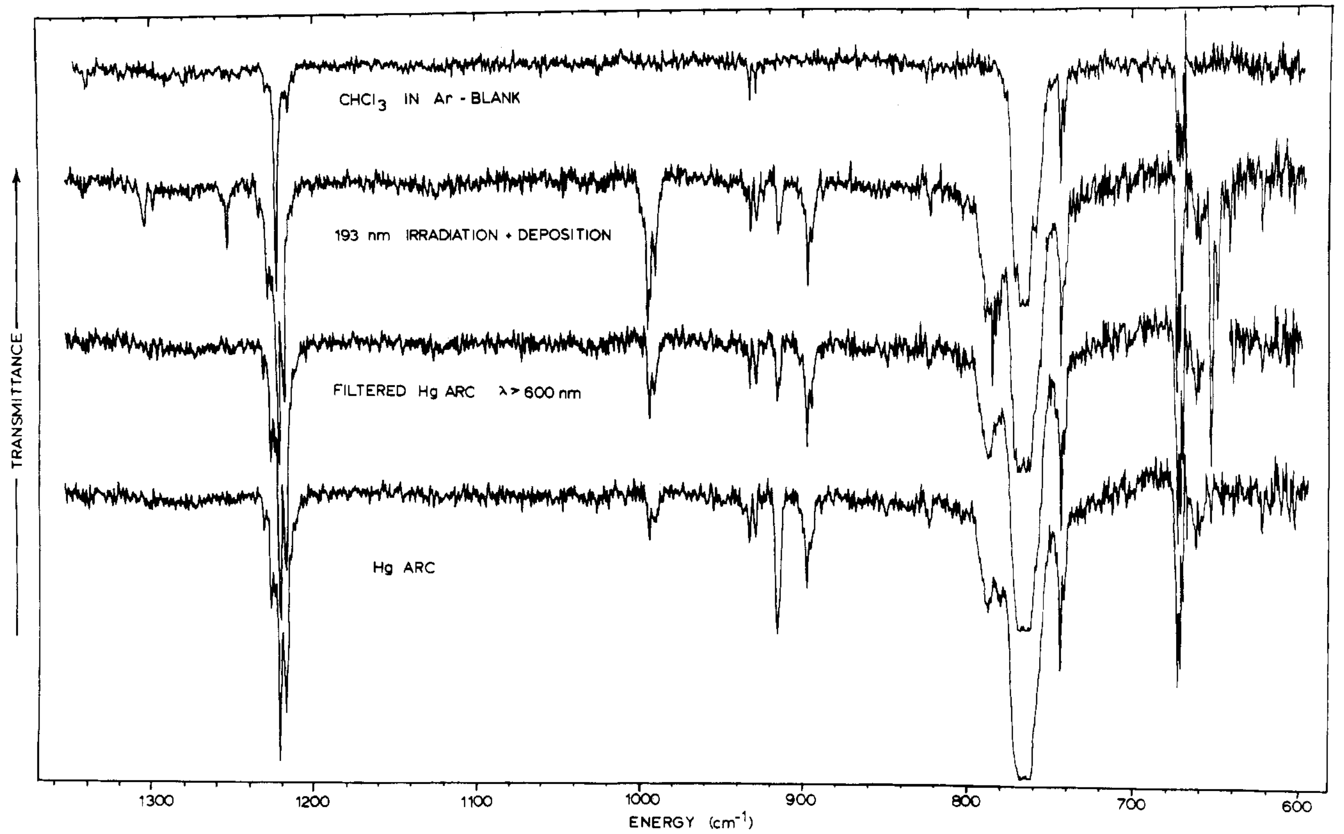

Figure 2. Infrared spectra for the $CHCl_3$ system in argon. The top trace shows a spectrum of the parent reagent. The second trace shows the spectrum obtained after 193-nm irradiation during deposition, while the third trace shows the outcome of subsequent filtered Hg arc irradiation (passing wavelengths greater than 600 nm). The bottom trace shows the results of the final Hg arc irradiation with only a H_2O filter.

the laser during deposition, the same two bands were observed in the final spectrum, with considerably increased intensity. The band at 763 cm^{-1} had 0.7 absorbance unit compared to 0.4 for the in situ experiment, while the band at 1103 cm^{-1} increased from 0.1 to 0.15 absorbance unit.

Discussion

Product Identification. CCl_4 Studies. Earlier studies[10,12,13] have subjected Ar/CCl_4 mixtures to windowless discharges and proton-beam irradiation, yielding a number of fragment neutrals and ions, all of which have been assigned. The reaction of CCl_4 with alkali-metal atoms has also been examined, and the spectra of product radicals were obtained.[42] As noted in the preliminary communication of this research,[26] the bands observed here match a number of the previously recorded absorptions very closely, including photoactivity upon Hg arc irradiation. Consequently, assignments can be made directly from these previous studies. The absorptions near 500, 926, 1011, and 1019 cm^{-1} in argon are all assigned to species derived directly from the CCl_4^+ cation trapped within the matrix cage. The band at 926 cm^{-1} has been attributed to a distorted (nontetrahedral) CCl_4^+, while the 1011- and 1019-cm^{-1} bands have been assigned to the CCl_3^+ cation trapped with a Cl atom in a single matrix site. The multiplet near 500 cm^{-1} has been assigned to the Cl_3^+ cation, trapped in the same matrix cage with the CCl diatomic. CCl, with a much lower absorption coefficient than the ions, has been seen previously near 850 cm^{-1} and may be responsible for the weak absorption near 853 cm^{-1} in the N_2 matrix experiments. The absorption at 898 cm^{-1} has been seen in numerous studies in the past and is due to the very stable CCl_3 radical. The additional absorptions that became quite pronounced in the simultaneous deposition/irradiation experiments at 683 and 915 cm^{-1} have been assigned to the C_2Cl_6 and C_2Cl_4 species. It is also noteworthy that while previous discharge and proton-beam radiolysis studies of CCl_4 led to an absorption at 1037 cm^{-1}, which was assigned to the isolated CCl_3^+ cation, this band was not observed in the present study.

The mechanism of product formation, particularly in the in situ irradiation experiments, is probably quite straightforward. The dissociative ionization of CCl_4 requires[27,43] roughly 12 eV, while a single photon at 193 nm supplies only 6.4 eV. Even with some ion solvation by the matrix environment, the ionization potential will not be lowered to 6.4 eV, where a one photon ionization might occur. Rather, the ionization process is very likely a two or more photon process, with the first photon promoting CCl_4 to an excited state (there are several near 6.4 eV) and the second photon bringing about ionization and the different fragments that were observed. Since the overall matrix must remain electrically neutral, the fate of the ejected electron must be considered. CCl_4 is also an effective electron trap,[44,45] dissociatively attaching an electron to form CCl_3 and Cl^-. A considerable yield of CCl_3 was detected, and the Cl^- anion is infrared invisible. These two species are likely trapped in the same matrix cage, with very slight, if any, perturbations to the CCl_3 radical. While the absorption coefficients of these different species are not known, it is likely that the cations absorb more strongly in the infrared than the neutral CCl_3, as a consequence of its greater dipole moment derivative during a given normal vibration. Consequently, the amount of CCl_3 formed is probably sufficient to account for all of the cations formed in these experiments. Direct formation of CCl_3 from chlorine atom detachment from CCl_4 is unlikely, particularly in the in situ irradiation experiments, where the chlorine atom would be unable to diffuse away and recombination would occur. Moreover, if the absorption at 898 cm^{-1} were due to isolated CCl_3, then one would anticipate photoionization of this radical to yield the isolated CCl_3^+ cation, which was not observed.[6] Rather, the 898-cm^{-1} absorption is best assigned to a CCl_3 radical cage paired with Cl^-. The

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898-cm^{-1} absorption has been assigned to the antisymmetric C–Cl stretching mode, which is an in-plane vibration and not likely to be sensitive to the presence of the Cl$^-$.

$CHCl_3$ Studies. Excimer laser irradiation of samples of Ar/$CHCl_3$ and Ar/$CDCl_3$ yielded a number of product absorptions, as given in Tables I and II, where grouping is also given by the wavelength dependence of Hg arc photolysis. None of the observed product bands attributable to the readily photobleached species A in the $CHCl_3$ experiments matched those in the $CDCl_3$ experiments, indicating that species A contains hydrogen. Since no new absorptions appeared in the mixed H/D experiments, a product that requires two hydrogens and hence proton migration is not likely. Moreover, the photobleaching behavior is indicative of ion formation. However, in contrast to the CCl_4 results, very few of the product bands observed here with 193-nm irradiation of $CHCl_3$ or $CDCl_3$ match product absorptions observed in the previous studies employing resonance discharge photolysis or alkali-metal atom reactions.[14–18,46] However, a very good match is noted to the bands assigned to the parent anions $CHCl_3^-$ and $CDCl_3^-$ in proton-radiolysis experiments,[19] namely the absorptions near 648 and 523 cm^{-1}, respectively. Both the deuterium shift and the photobleaching behavior are consistent with this assignment. While $CHCl_3^-$ was a minor product in the proton radiolysis of $CHCl_3$, it appears in the present experiments as the major product and in very good yield. The other product bands labeled A in Tables I and II can be likewise assigned to this anion, including absorptions at 1252, 1304, and 3087 cm^{-1} in the $CHCl_3$ experiments. These most likely escaped detection in the proton-radiolysis experiments due to the significantly lower product yield in those experiments.

Little is known about the $CHCl_3^-$ anion, other than the fact that it is quite unstable under laboratory conditions,[14,19,47–49] which is consistent with photobleaching with red or near-infrared light. Dissociative electron attachment to $CHCl_3$ is well-known, and the mechanism proposed for the formation of the anion is through recombination of radical and anionic fragments. The high yield of the anion in the present study suggests that the current matrix conditions are quite effective for this recombination, a result that has played a major role in the excimer laser photochemistry of other compounds.

Relatively little is known about the structure of anions of this general formula. ESR studies of the CF_3X^- (X = Cl, Br, I) species indicated that the three fluorines were equivalent, such that the C_{3v} symmetry was maintained.[50,51] On the other hand, studies of the anions of CBr_4, $CHBr_3$, and $RCBr_3$ suggested a high degree of distortion from a tetrahedral structure.[52] Some inference can be made as to the structure of the $CHCl_3^-$ anion from the spectral data obtained here. One might expect the C–H bond to be weakened upon addition of an electron to $CHCl_3$, yet the C–H stretching frequency in $CHCl_3^-$, at 3087 cm^{-1}, is greater than for parent $CHCl_3$. Since the C–H force constant is probably not increasing, the effective reduced mass of the vibration must be decreasing, suggesting a change in structure going from the neutral parent to the anion. The 648-cm^{-1} absorption and its 523-cm^{-1} deuterium counterpart were assigned previously to the a C–Cl stretching vibration. The significant deuterium shift of this mode (H/D = 1.23) suggests considerable hydrogen contribution to the vibration, much more so than in the parent species, where a ratio, H/D = 1.03, was observed. This, too, argues for significant distortion from the parent geometry. The bands at 1252 and 1304 cm^{-1} fall in a region expected for the Cl–C–H bending mode, as well as the overtone of the 648-cm^{-1} stretching band. Both modes show considerable deuterium shifts, to 1038 and 1060 cm^{-1}, and while definite assignment is not readily made, the two bands are likely due to Fermi resonance between these two modes. The nature of the distortion from the parent geometry is less clear, although the $CHBr_3^-$ studies[52] would suggest an SF_4-like structure. No firm conclusions on this point may be drawn from the current results, although some distortion is apparent.

The species labeled C in Tables I and II were insensitive to photobleaching and can be assigned to more stable species. The broad absorptions near 2800 and 2040 cm^{-1} in the $CHCl_3$ and $CDCl_3$ experiments can readily be assigned to HCl and DCl in weakly hydrogen-bonded complexes.[22,53] The absorption labeled D in Table I actually grew slightly upon Hg arc irradiation, indicating that it is a relatively stable species and probably formed through a recombination process. An absorption was noted in this region in the above CCl_4 studies and was assigned to C_2Cl_4; similar assignment here is likely. This band was not observed in the $CDCl_3$ experiments, but this spectral region was obscured by an intense parent mode.

Several additional bands labeled C in Table I match product absorptions observed in the previous high-energy irradiation and proton-radiolysis studies of $CHCl_3$. For example, a band at 898 cm^{-1} has been assigned[42,46] to both the $CHCl_2$ and CCl_3 radicals, while the band at 1219 cm^{-1} has been assigned to $CHCl_2$. However, the corresponding bands were not observed in the present $CDCl_3$ experiments. This suggests that either the present product bands at these locations must be assigned to different species or the photochemical reactions of $CHCl_3$ and $CDCl_3$ are somewhat different. While neither alternative is particularly appealing, the latter is more likely, particularly given the different number of product absorptions in the $CHCl_3$ and $CDCl_3$ experiments.

Several bands listed in Table I, labeled B, showed intermediate photobleaching activity; they decreased with continued irradiation but at a slower rate than the $CHCl_3^-$ anion. The best assignment is to a relatively unstable species, possibly a molecular cation, but one that is more stable than $CHCl_3^-$. An absorption was observed at 998 cm^{-1} in previous proton radiolysis studies,[19] where the overall yield was much less than in the present work, but not in the corresponding discharge experiments. In the proton radiolysis experiments, this band was assigned to the $CHCl_2^+$ cation, but later discharge studies[16,20] have instead assigned bands near 1045 cm^{-1} to this isolated cation. One possibility is assignment to the parent cation $CHCl_3^+$, which has previously escaped detection, although the $CHCl_2^{\bullet+}Cl$ cation has been observed.[16] Definitive identification of this species cannot be made at present, but a molecular cation is the most likely candidate. The multiplet near 785 cm^{-1} may well be assigned to less intense absorption of this same cation that escaped detection in previous proton-radiolysis studies. One corresponding type-B band was observed at 794 cm^{-1} in the $CDCl_3$ experiments, in a position appropriate for a deuterium counterpart of the 995-cm^{-1} product absorption in the $CHCl_3$ experiments. A band at 798 cm^{-1} was observed in previous discharge studies[16] of $CDCl_3$ in argon and assigned to $CDCl_2{\bullet}Cl^-$. While such an assignment is possible here, the corresponding species $CHCl_2{\bullet}Cl^-$, which absorbs at 838 cm^{-1}, was not observed in the present study. On the other hand, assignment to the molecular cation also helps resolve the question as to the location of the positive charge in the matrix, to offset or neutralize the negative charge of $CHCl_3^-$.

CH_2Cl_2 Studies. The major product band in the CH_2Cl_2 studies at 763 cm^{-1} has been seen previously in matrix ionization studies[12–15] and has been assigned to the methylene chloride parent cation $CH_2Cl_2^+$. Earlier workers reported a second band, at 1193 cm^{-1}, for this species that was not observed here, perhaps due to insufficient yield. The earlier studies also reported a number of secondary fragment species, both neutrals and ions, which were not observed in the present study. The weak band at 1103 cm^{-1} was insensitive to photobleaching, indicating that it is due to a relatively stable species, which cannot be readily assigned by

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comparison to previous studies.

Photophysical Aspects. The previously reported excimer laser photolysis studies[23–26] demonstrated that the laser does penetrate fully the matrix, so that the drop-off in yield after a few minutes of irradiation is not a surface phenomenon. This point is substantiated by the observation here that the yield of product was dependent on the amount of sample deposited for in situ irradiation experiments. Further, the relative insensitivity of the product yield to laser repetition rate demonstrates that the photolysis is not occurring in the gas phase prior to deposition. At the same time, the increased yield when irradiation was conducted during deposition indicates that higher conversion to product occurs (for these systems) when the parent molecules are not rigidly trapped within the matrix cage. This cage effect has been shown to vary in importance depending on the species involved.[24] Finally, the data obtained did not allow determination of the photon or power dependence of the photolysis process in that virtually the same yield of product was observed for a given irradiation time and repetition rate, *independent of laser power.* This is most likely a consequence of matrix cage restrictions on the photochemical processes, surface scattering difficulties, and possibly absorption by the newly formed products within the matrix.

Conclusions

The feasibility of carrying out excimer laser photoionization at 193 nm in inert matrices, for processes requiring two or more photons, has been demonstrated. The products isolated in these experiments have generally been observed in previous proton-beam radiolysis and windowless discharge experiments but only during the deposition process. Excimer laser irradiation does offer several advantages over discharge and radiolysis techniques, including the ability to carry out the energy deposition process in situ. This, in turn, leads to a greater yield of primary photoproduct and fewer secondary reaction products, and consequently a cleaner spectrum. In the CCl_4 studies, largely cage pairs were formed and recombination processes played an important role in these experiments.

Laser irradiation during deposition generally enhanced product yield, consistent with the idea that surface species have more mobility and are not constrained by the matrix cage. Observation of radical–radical recombination products, e.g., C_2Cl_6, when the samples were irradiated during deposition but not when the sample was irradiated after deposition supports this hypothesis. The variation of laser power and repetition rate over a substantial range did not cause much change in product yield in these experiments, so that the power dependence of ion formation could not be determined. Finally, the results obtained here demonstrate that excimer laser photochemistry under matrix isolation conditions is not a surface layer phenomenon but can occur throughout the rigid matrix.

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Registry No. CCl_4, 56-23-5; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; D_2, 7782-39-0; $CHCl_3^-$, 57029-22-8.

Chemiluminescence during the Reaction of Molecular Fluorine and Carbon Diselenide: Emission from Se_2, SeF, and an Unknown Emitter[†]

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The gas-phase chemiluminescence spectrum between 3500 and 8800 Å from the reaction of F_2 with CSe_2 has been studied at pressure conditions near 1 Torr and a resolution of 2 Å. Vibrationally resolved bands can be ascribed to $SeF(A^2\Pi_{3/2}–X^2\Pi_{3/2})$ and to $Se_2(A^3\Pi_u–X^3\Sigma_g^-)$ and $Se_2(B^3\Sigma_u^-–X^3\Sigma_g^-)$ on the basis of comparison with their known positions. Emission from these features occurs over only a narrow range of reaction conditions. An apparently new broad-band feature, unresolved at this resolution, is observed to extend from 6000 Å to the near-IR region. The results are contrasted with those from the reaction of F_2 with CS_2.

A systematic search is under way in this lab to find novel emission spectra of reactive small molecules generated during the reactions of molecular fluorine with sulfur,[1] selenium,[2] and tellurium[3] compounds. In a previous paper the results of a study of the chemiluminescence from the reaction of F_2 with CS_2 were presented.[4] A novel vibronic band system was observed extending from 5510 to beyond 9000 Å. Spectra were obtained at better than 0.5-Å resolution and clearly showed two long progressions in 356 and 831 cm^{-1}. It was suggested that the spectrum was due to a new small molecule containing only C, F, and/or S.[4] In order to obtain comparable information, the reaction of F_2 with CSe_2 was studied under similar conditions.

The reaction was carried out in a 1.5-L pumped reaction chamber as described previously.[1,5] A 10% fluorine in helium mixture was used as obtained from Air Products. Carbon diselenide, containing ~5% methylene chloride, was obtained fresh from Strem Chemicals. As much of the CH_2Cl_2 as possible was removed by pumping on the sample during several freeze/thaw cycles. The chemiluminescence was dispersed by a McPherson Model 207, $^2/_3$-m scanning monochromator. A 110 × 110 mm holographic grating of 1800 lines/mm gave the spectrometer an aperture of *f*/5.8 and a dispersion of 8.3 Å/mm. The instrument was calibrated against a low-pressure neon lamp. Detection was done by a dry ice cooled GaAs photomultiplier tube (Hamamatsu R943-02) bathed in dry N_2. The PMT signal was sent to a picoammeter and then to a chart recorder. The emission, and

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[†] Dedicated to Dr. Gerald L. Simmons on his retirement from teaching.

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