Matrix Photoionization of Methyl Halides. Ultraviolet Spectra of the Parent Cations and Infrared Evidence for Intramolecular Hydrogen-Bonded Parent Anions in Solid Argon

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Abstract: Methyl halide samples were subjected to argon discharge photoionization during deposition at 15 K. New ultraviolet absorptions at 255, 335, 348, and 373 nm assigned to the CH_3X^+ cations (X = F, Cl, Br, I) in solid argon correlate with differences between photoelectron bands. New infrared absorptions in CH_3F experiments identify both type I and type III intramolecular hydrogen-bonded parent anions formed upon fluoride ion elimination.

Introduction

Recent matrix spectroscopic studies of carbon tetrahalides and methylene halides subjected to argon resonance photoionization have provided infrared and visible–ultraviolet spectra of the parent cations CX_4^+ and $CH_2X_2^+$ (X = Cl, Br).[1-3] The photochemistry of the matrix-isolated cations was consistent with gas phase appearance potential data, and the electronic absorption spectra were correlated with photoelectron spectra. A similar investigation of $CHCl_3$ and $CHBr_3$ gave infrared spectra of a stable electron capture product identified as the type I intramolecular hydrogen-bonded X^--HCX_2 parent anion[4,5] and the corresponding study of CHF_3 produced the type III F–H—$(CF_2)^-$ species[6] illustrating the role of different halogens on the nature of the hydrogen bonding. In order to complete this study, the analogous experiments were performed on all of the methyl halides.

Methyl halide cations have been examined in the gas phase using electron impact,[7,8] photoionization,[9-11] photoelectron spectroscopy[12-14] and ion photodissociation.[15-18] The photodissociation curves of CH_3Cl^+ in two of the latter[15,16] studies are of particular interest as they are related to the absorption spectrum of these ions in solid argon.

Experimental Section

The cryogenic apparatus and matrix photoionization methods have been described.[1,19] Reagent gases CH_3F, CH_3Cl, CH_3Br (Matheson), and CH_3I (Eastman Organic Chemicals) were condensed at 77 K and evacuated before preparing Ar/CH_3X = 200/1 to 400/1 mixtures using standard vacuum techniques. Isotopic precursors ($^{13}CH_3F$, 90% C-13, and CD_3Br) were obtained from Merck Sharpe and Dohme. Samples of CD_3F and CD_3Cl were prepared by reacting CD_3Br with HgF_2 and $HgCl_2$ at about 200 °C for several hours. These samples were deposited onto a CsI substrate at 15 K for infrared or a sapphire window at 22 K for optical studies at rates near 2 mM/h during simultaneous exposure to argon discharge radiation from windowless resonance lamps[20] which codeposited an approximately equal amount of argon with the sample. Infrared spectra were recorded during and after 16–20-h deposition and photoionization with a 10-mm orifice discharge tube using expanded wavenumber scale of a Beckman IR-12, and optical spectra were taken on a Cary 17 after 2–4 h of sample deposition using 3-mm diameter orifice discharge lamps. Similar spectra were recorded after 30-min filtered photolysis periods using a high pressure mercury arc (Illumination Industries, Inc.).

Results

Infrared and ultraviolet-visible spectra of methyl halide matrix systems will be described.

Infrared Spectra. Three photoionization experiments and a sample blank were done with Ar/CH_3F = 300/1 and 400/1 samples, and the spectra are similar to those reported by Jacox and Milligan (JM),[21] although yields in the present longer experiments were somewhat higher; for example, the 1181-cm^{-1} CHF band was observed with A = absorbance units = 0.70 and the 1163-cm^{-1} CH_2F absorption was observed at A = 1.3. Additional bands in the present experiments at 1226, 1417, and 1427 cm^{-1} are due, respectively, to SiO and SiO_2 from the quartz discharge tube.[22,23] A weak band at 1150 cm^{-1} that grew markedly at the expense of CF at 1275 cm^{-1} on sample warming can be assigned to C_2F_2.[24] A strong, sharp product band at 275 cm^{-1} in all experiments showed no isotopic shifts and is not identified. Sharp weak product bands at 3266, 2569, and 2164 cm^{-1} with C-13 counterparts at 3259, 2538, and 2117 cm^{-1} are not assigned. A final sharp product feature at 1441 cm^{-1} in the CH_3F studies was stable to photolysis; without isotopic counterparts, no identification is possible. A broad feature due to CH_3 radical was observed at 619 cm^{-1} (A = 0.02) with a C-13 counterpart at 614 cm^{-1} (A = 0.02).[25]

Three sets of new product bands observed in the present CH_3F experiments at 3530 (about 16-cm^{-1} full width at half-maximum) and 3498 cm^{-1} (A = 0.10), 2664 cm^{-1} (about 7-cm^{-1} FWHM, A = 0.10) and 390 cm^{-1} with a 378 cm^{-1} counterpart (A = 0.12) are shown in Figure 1a. Photolysis for 60 min with 220–1000-nm radiation had no effect on the higher wavenumber absorptions; however, the 390-cm^{-1} component grew slightly on photolysis and the 378-cm^{-1} component decreased, with the overall intensity remaining approximately constant.

The isotopic experiments are also contrasted in Figure 1. The upper and lower doublet bands exhibited no measurable carbon-13 shift, whereas the 2664-cm^{-1} absorption showed a definite carbon-13 shift to 2655 cm^{-1} (A = 0.13). The product absorptions exhibited large deuterium shifts; deuterium counterparts were observed at 2597 and 2575 cm^{-1}, 1982 cm^{-1} with a satellite at 1971 cm^{-1}, and 305 cm^{-1}. An additional feature in the CD_3F spectrum at 2563 cm^{-1} was destroyed by photolysis. A strong, sharp 644 cm^{-1} absorption observed (A = 0.48) in the CD_3 F study was reduced (A = 0.40) on full arc photolysis; this feature is probably due to Ar_nD^+.[26,27] The CD_3 radical was observed at 463 cm^{-1} (A = 0.02).[25]

Two methyl chloride photoionization experiments were done using 400/1 and 1000/1 concentrations. The spectra are similar but more intense than those of JM.[28] Two matrix sites of the CH_2Cl radical were observed, one with sharper absorptions at 1391, 826, 820, and 397 cm^{-1} (A = 0.06, 0.17, 0.05, 0.32, respectively) that were observed in the previous lithium atom matrix reaction study[29] and slightly broader absorptions at 1394, 839, 833, and 402 cm^{-1} (A = 0.04, 0.13,

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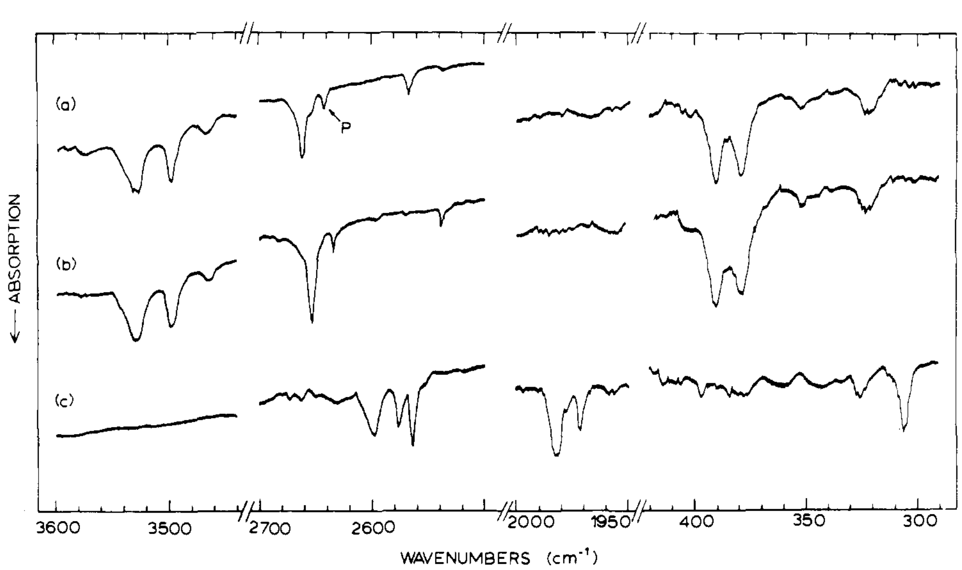

Figure 1. Infrared spectra on expanded wavenumber scale in regions of new product absorptions recorded after condensation of Ar/CH_3F = 300/1 samples for 16-20 h at 15 K with argon resonance photoionization from a 10-mm i.d. discharge tube. (a) CH_3F, (b) $^{13}CH_3F$, 90% C-13, and (c) CD_3F. P denotes a CH_3F precursor absorption.

0.03, 0.22). Site and chlorine isotopic splittings were observed for CCl at 871, 866, and 860 cm^{-1}; photolysis favored the upper site. Analogous behavior was found for CHCl split bands at 814 and 811 cm^{-1}. No new photosensitive bands were observed in the 800-1000-cm^{-1} region that could be due to the parent cation.

Sharp new bands were observed at 2819 and 2808 cm^{-1}; the latter grew and the former decreased on photolysis. A weak, broad band was found at 2750 cm^{-1} (A = 0.03, 10-cm^{-1} fwhm) which showed no photolysis effect. Two experiments were done with a 300/1 CD_3Cl sample; the spectrum resembled that of JM,[28] including a weak 2038-cm^{-1} band (A = 0.03, 10-cm^{-1} fwhm).

Experiments were done with CH_3Br and CD_3Br. Again the major product was CH_2Br radical at 1356, 693, and 367 cm^{-1} (A = 0.12, 0.10, 0.20, respectively) and CD_2Br at 1016, 656, and 263 cm^{-1} (A = 0.11, 0.04, 0.11, respectively).[30] The Ar_nD^+ absorption was observed at 644 cm^{-1} (A = 0.07). No new photosensitive product bands were observed.

Ultraviolet-Visible Spectra. Two experiments were done with Ar/CH_3F = 400/1 samples and the 3-mm diameter discharge tube; both studies revealed a weak, broad absorption centered at 255 nm (A = 0.02) above the rising sample background. The absorption was destroyed with 290-1000-nm photolysis, as is shown in Figure 2a. In addition, weak CHF absorptions were observed at 443, 466, and 494 nm in good agreement with JM.[21]

Two studies were performed with Ar/CH_3Cl samples and the 3-mm discharge tube which produced a broad 335-nm band (A = 0.04) above the sample background; these features were destroyed by 30 min of 290-1000-nm photolysis, which is illustrated in Figure 2b. Similar studies using 200/1 samples and the 10-mm diameter discharge tube produced a comparable 335-nm absorption, but the sharp 279-nm CCl radical absorption[28] was increased fourfold.

A set of two studies was done with Ar/CH_3Br = 400/1 samples and the 3-mm tube. The spectrum from one of these runs is shown in Figure 2c; new product bands were observed at 267 nm (A = 0.10), 348 nm (A = 0.21), and 600 nm (A = 0.02). Photolysis with 500-1000-nm light for 55 min reduced the bands to 267 nm (A = 0.07), 348 nm (A = 0.15), and 600 nm (A = 0.00), and a like exposure to 290-1000-nm light continued this trend to 267 nm (A = 0.02) and 348 nm (A = 0.05); the latter spectrum is illustrated by the dashed trace in Figure 2c.

A similar pair of experiments was done with Ar/CH_3I = 400/1 samples; the spectrum is shown in Figure 2d. The 255-nm CH_3I parent band was observed before sample photoionization. A weak product band at 285 nm (A = 0.07) on the steep sample background was not affected by photolysis. The dominant new absorption was centered at 373 nm (A = 0.15), and a weak broad band was observed at 455 nm (A = 0.02). Photolysis with 650-1000-nm radiation for 30 min did not change the bands, 500-1000-nm irradiation reduced 373 nm (A = 0.12) and 290-1000-nm light reduced the major band slightly 373 nm (A = 0.10), while the 455-nm absorption was not changed; the latter spectrum is shown in the dashed trace in the figure.

Discussion

The ionization energies of CH_3F, CH_3Cl, CH_3Br, and CH_3I are 12.7, 11.3, 10.5, and 9.5 eV, respectively.[13,14] The major output of the windowless argon discharge lamp is the 11.6-11.8-eV argon resonance doublet which is adequate for photoionization of the three heavier methyl halides. At lower argon pressures, the 10-mm diameter orifice tube has a substantial output in the 13-15-eV range[29] which is capable of photoionizing CH_3F. The product spectra were analyzed with these and other charged products in mind.

Optical Spectra. Figure 2 contrasts broad product absorptions in the methyl halide spectra at 255, 335, 348, and 373 nm with increasing size of X. The absorptions were photosensitive with increasing difficulty of dissociation as the size of X increases making halogen escape from the matrix cage and photodissociation more difficult. Photoionization yield data show that dissociation of the CH_3X^+ ions (X = Cl, Br, I) to CH_3^+ and X requires 2.5 ± 0.2 eV, whereas CH_3F^+ gives CH_2F^+ at 0.9 eV and CH_3^+ at 3.8 eV.[10,17] Since these threshold energies are exceeded by the mercury arc energy, the photosensitive ultraviolet product absorptions observed here are assigned to the parent cations CH_3X^+. The matrix absorption maxima for the methyl halide cations are near the methylene halide cation absorptions which are compared in Table I.

The broad 255-nm absorption for CH_3F^+ is in good agreement with the energy difference between the first two photo-

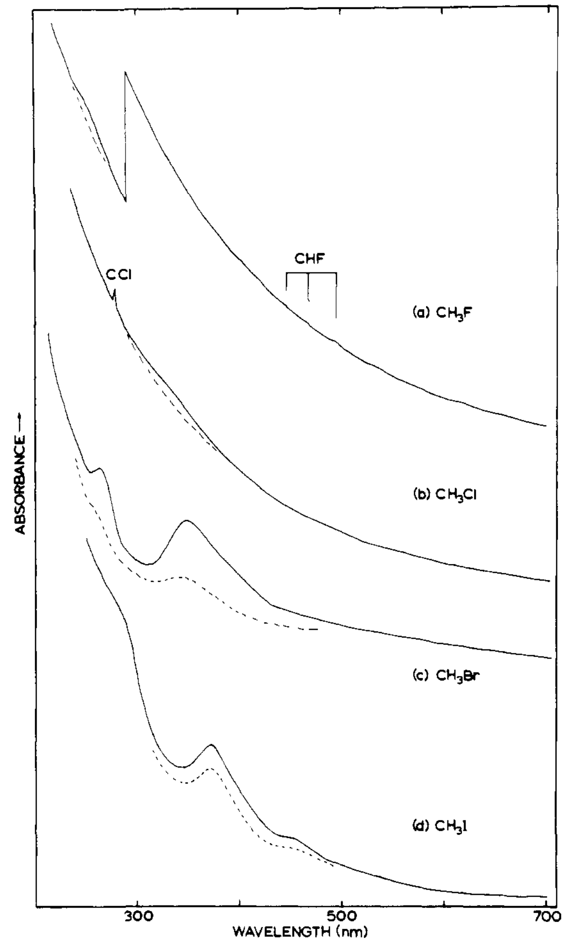

Figure 2. Ultraviolet-visible spectra recorded after condensation of Ar/CH_3X = 400/1 sample for 2-4 h at 22 ± 2 K under exposure to argon resonance radiation from a 3-mm i.d. discharge tube. (a) CH_3F, step in spectrum is due to suppression, (b) CH_3Cl, (c) CH_3Br, and (d) CH_3I. The dashed traces were recorded after 30 min of 290-1000-nm photolysis.

electron (PES) bands. The first ionization of CH_3F at 12.7 eV removes a CH_3 (π_e) bonding electron, and the second ionization at 17.1 eV has been ascribed to a fluorine lone pair electron.[14] The energy difference, 4.4 eV, corresponds to a 282-nm transition between the above electronic states of the ion, which is near the onset of the observed broad band peaked at 255 nm.

The broad 335-nm absorption for CH_3Cl^+ is in very good agreement with the CH_3Cl^+ photodissociation spectrum which gave a peak CH_3^+ production at 315 nm.[15,16] The broad matrix absorption begins near 400 nm which corresponds with the 3.1-eV energy difference between the first Cl lone-pair ionization at 11.3 eV and the C-Cl (σa_1) bond ionization at 14.4 eV.[14] The matrix absorption probably contains a contribution from the electronic state of the ion reached by the 15.3-eV PES band attributed to ionization of a $CH_3(\pi_e)$ bonding electron,[14] which corresponds to a 310-nm transition from the ground state ion. The argon matrix has apparently broadened these two electronic transitions for CH_3Cl^+ into a single broad absorption. This is not surprising in view of the incomplete resolution of these two bands in the PES of methyl chloride.[13,14]

Two absorptions in the methyl bromide experiment at 348 and 267 nm are assigned to CH_3Br^+. The onset of the major absorption near 420 nm corresponds to the energy difference between the first bromine lone pair ionization at 10.5 eV and the C-Br bond ionization at 13.5 eV,[14] although the matrix absorption peaks to slightly higher energy at 348 nm. The 267-nm absorption corresponds exactly with the difference between the first 10.5 eV and third $CH_3(\pi_e)$ ionization energy at 15.2 eV. The resolution between the two bands for CH_3Br^+ is increased relative to CH_3Cl^+ since the first two ionizations are halogen dependent and decrease 0.8-0.9 eV for bromine, whereas the $CH_3(\pi_e)$ orbital is halogen independent. These bands are also better resolved in the PES of methyl bromide.[13,14]

Table I. Ultraviolet Absorptions (nm) for Methyl and Methylene Halide Cations in Solid Argon at 22 ± 2 K

X	CH_3X^+	$CH_2X_2^+$
F	255	
Cl	335	342[a]
Br	267, 348	362
I	373	375

[a] Reference 3.

Only one photosensitive product absorption, 373 nm, was observed for CH_3I^+ since the higher energy band is expected near 234 nm where the sample background is too steep to locate another absorption. The onset of the major absorption near 420 nm in solid argon is to slightly higher energy than the 500 nm onset of the photodissociation of the ground state ion in the gas phase.[18] The beginning of the matrix absorption corresponds to the difference between the first I lone pair ionization at 9.5 eV and the C-I bond at 12.5 eV,[14] although, as in the CH_3Br^+ case, the product band peaks to higher energy, at 373 nm.

Infrared Spectra. The infrared spectra were searched for photosensitive absorptions that could be assigned to parent cations, but none were found. Apparently, the concentration of parent cations in the matrix samples was below the present limit for infrared detection. Parent ions observed in previous experiments contained two or more halogens which provided antisymmetric carbon-halogen stretching vibrations that produce more intense vibrations than single C-X bond stretching modes.

Three sets of new product absorptions in the CH_3F study correlate with previous observations for intramolecular hydrogen-bonded parent anions. The 3530, 3498, 390, and 378 cm^{-1} absorptions have the common vibrational characteristic of large deuterium shifts and no carbon-13 shift, which indicates that the vibrations involve hydrogen but not carbon. This is reminescent of strong bands at 3599, 3562, 603, and 562 cm^{-1} in analogous CHF_3 studies, which were assigned to the type III electron-capture photolysis product $F-H—(CF_2)^-$ formed upon proton abstraction by the eliminated fluoride ion. The upper absorptions were assigned to the H-F stretching mode and the lower bands to the hydrogen deformation mode split by differing structures or matrix sites. The new 3530, 3498, 390, and 378 cm^{-1} absorptions are assigned to the analogous $F-H—(CH_2)^-$ complex. Table II contrasts the vibrational data for several intramolecular hydrogen-bonded complexes. The H/D isotopic ratios for the two bands, 3530/2597 = 1.3593 and 3498/2576 = 1.3579, are comparable to the fluoroform product values 3599/2653 = 1.3571 and 3562/2625 = 1.3564. The H/D ratios for the H-F hydrogen-bonded complexes are below the HF/DF = 3962/2896 = 1.3681 value,[31] which denotes more anharmonicity in the complex where the H-F stretching vibration is shifted to lower wavenumber by hydrogen bonding.

The 2664-cm^{-1} product band, on the other hand, exhibited a definite carbon-13 shift to 2655 cm^{-1} and a deuterium shift to 1982 cm^{-1} which denotes a C-H stretching vibration. The H/D ratio 2664/1982 = 1.3441 is comparable to that of CHF_3/CDF_3 = 3049/2263 = 1.3473. Since the C-H stretching modes of CH_3F appear at 3022 and 2972 cm^{-1}, a

Table II. Infrared Absorptions (cm^{-1}) Assigned to Intramolecular Hydrogen-Bonded Molecular Anions

	Type III	
$F\text{-}H—(CF_2)^-$	$F\text{-}H—(CH_2)^-$	$F\text{-}H—(CHF)^-$
3598, 3562[a]	3530, 3498	3243, 3124[b]
603, 562	390, 378	847, 803
	Type I	
$F^-—HCH_2$	$Cl^-—HCCl_2$	$I^-—HCCl_2$
2664	2723[c]	2863
$Cl^-—HCH_2$	$Br^-—HCCl_2$	
2750	2795	

[a] Reference 6. [b] Andrews, L.; Prochaska, F. T. *J. Chem. Phys.* **1979**, *70*, 4714. [c] References 4 and 5.

C-H stretching mode at 2664 cm^{-1} requires a substantial perturbation.

The type I hydrogen-bonded complexes $I^-—HCCl_2$, $Br^-—HCCl_2$ and $Cl^-—HCCl_2$ exhibited C-H stretching modes at 2863, 2795, and 2723 cm^{-1}, respectively, which show larger displacements in the C-H mode with increasing proton affinity of the perturbing halide ions.[4,5] The 2664-cm^{-1} absorption exhibits the correct isotopic shifts for a C-H stretching mode and the band position nicely fits the above type I trend for a fluoride species. Accordingly, the 2664-cm^{-1} absorption is assigned to $F^-—HCH_2$, which is unique among fluoride species as the only example of a type I complex among the fluoromethanes.

The two CH_3F fluoride elimination products proposed here differ only in the nature of the hydrogen bonding. Since the type of hydrogen bonding is determined by the proton affinities of the two opposing groups,[32] the present observation of both types of hydrogen bond for the same molecular species suggests an activation energy for proton abstraction from CH_3 radical. This energy is provided to some of the $(F^-)(CH_3)$ ensembles in the matrix by the discharge lamp leading to proton abstraction and the type III species $F\text{-}H—(CH_2)^-$, and others give the type I complex $F^-—HCH_2$.

Weak bands observed in CH_3Cl and CD_3Cl experiments at 2750 and 2038 cm^{-1} are tentatively assigned to the type I species $Cl^-—HCH_2$ and $Cl^-—DCD_2$. This possible identification of the CH_3Cl chloride elimination product is supported by the observation of similar C-H and C-D stretching modes at 2723 and 2059 cm^{-1}, respectively, for $Cl^-—HCCl_2$ and $Cl^-—DCCl_2$.[4,5]

Conclusions

Methyl halide samples were subjected to argon resonance photoionization during condensation at 15 K. Ultraviolet absorption spectra revealed new absorptions at 255, 335, 348, and 373 nm for the CH_3X^+ cations (X = F, Cl, Br, I). These absorptions were photolyzed by 290–1000-nm light in accord with dissociation data on the gaseous ions. The positions of the ultraviolet absorptions correlate with photoelectron spectra. Infrared spectra in CH_3F experiments revealed new absorptions at 3530 and 390 cm^{-1} with no C-13 and large D shifts which are consistent with the electron capture photolysis product type III hydrogen-bonded species $F\text{-}H—(CH_2^-)$. An additional band at 2664 cm^{-1} exhibited a C-13 shift to 2655 cm^{-1} expected for a C-H stretching mode which is appropriate for the type I complex $F^-—HCH_2$. The large displacement of the C-H stretching mode is expected for the very strong hydrogen bonding of fluoride ion.

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