Matrix Photoionization and Radiolysis of CH_2Cl_2 and CH_2Br_2. Infrared and Ultraviolet Absorption Spectra and Photolysis of $CH_2Cl_2^+$ and $CH_2Br_2^+$

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Abstract: Matrix photoionization and radiolysis of methylene chloride and bromide produced and isolated the $CH_2X_2^+$ and CHX_2^+ ions for spectroscopic and photochemical study. The antisymmetric vibrations observed for the parent ions show unusual isotope shifts, which are explained by spin-orbit interaction of the lowest two electronic states of $CH_2X_2^+$ formed by removal of halogen nonbonding electrons. The major ultraviolet absorption to an excited electronic state of each ion nicely correlates with photoelectron spectra. The parent ions photodissociated with red-visible light, which is in accord with their limited stability in the gas phase. Ultraviolet photolysis of these matrix samples produced infrared spectra of the isolated CHX_2^+ ions, CHX_2 radicals, and the matrix solvated proton Ar_nH^+.

The absorption spectroscopy of molecular cations is of growing interest, with such techniques as ion cyclotron resonance and photoelectron spectroscopy available to study gaseous cations. Argon resonance photoionization of a precursor molecule during condensation with argon at 15 K provides a means to produce and trap molecular cations for spectroscopic and photochemical examination.[1] In a study of the CF_3X molecules, infrared absorption and photolysis data were obtained for the CF_3^+, CF_2X^+, and CF_3X^+ molecular cations.[2]

Photoionization and fragmentation of the chlorinated and brominated methanes have been extensively investigated.[3,4] Methylene chloride and bromide are good candidates for a matrix-isolation study since the parent ions $CH_2X_2^+$ have been observed in the gas phase,[4-6] and the daughter ions CHX_2^+ have been produced in previous matrix work with the haloforms.[7,8] We report here the infrared and ultraviolet spectroscopic observation of the parent ions and their photochemical changes in argon matrices at 15 K.

Experimental Section

The cryogenic and vacuum systems and discharge photoionization sources have been described previously.[1,9] Reagent grade CH_2Cl_2, CH_2ClBr, CH_2Br_2, and CH_2I_2 and isotopic compounds CD_2Cl_2, CD_2Br_2, and $^{13}CH_2Cl_2$ (90% ^{13}C, Merck Sharpe and Dohme) were condensed, outgassed, and diluted with argon (Air Products, 99.995%) to give $Ar/CH_2X_2 = 400/1$ mixtures. These samples were deposited at 2 mmol/h on a 15 K CsI window for 20 h with a comparable amount of argon flowing through a 12-mm o.d. discharge tube. The argon emission was exposed to the sample through a 1-mm i.d. orifice. Since a comparable amount of additional argon was codeposited with the samples, the actual Ar/CH_2X_2 ratio was double the sample value.

Infrared spectra were recorded during and after sample deposition through a Kodak 220 far-IR transmitting filter placed in the source compartment of a Beckman IR-12. Expanded wavenumber scale spectra were recorded before and after photolysis with a high-pressure mercury arc (General Electric, BH-6) using water and Pyrex and Corning glass filters. Band positions are accurate to ± 0.5 cm^{-1}.

Additional experiments with each compound employed 2-keV proton beam radiolysis of the sample during condensation followed by recording infrared spectra, exposing the sample to a heated light bulb filament inside the vacuum chamber, and recording final spectra.[10] Previous experiments have shown that the heated filament acts as a weak visible photolysis source.[1] A sample of each compound was deposited without photoionization or radiolysis to measure the precursor and any impurity absorptions; these bands are labeled P in the figures.

Complementary photoionization experiments were performed using the optical absorption apparatus.[11] Samples were deposited for 1-3 h on a sapphire plate at 20 K exposed to the argon discharge through a 3-mm i.d. orifice. Absorption spectra were recorded from 2600 to 200 nm on a Cary 17 Spectrophotometer before and after filtered mercury arc photolysis. Band positions were measured at the wavelength equally dividing the integrated absorption above the background and are accurate to ±2 nm.

Results

Infrared experiments for each precursor molecule and ultraviolet absorption studies for the methylene halides will be described.

CH_2Cl_2. Argon-methylene chloride mixtures were deposited at 15 K with simultaneous exposure to the argon discharge emission for 20 h. Infrared spectra of these samples in regions of interest are shown in Figure 1a and the product bands are listed in Table I. New features of special interest are the bands labeled P^+ at 764 and 1194 cm^{-1}, and the 1045.4, 1042.5, 1039.8 cm^{-1} triplet and 1292.0 cm^{-1} absorption labeled R^+. Absorptions labeled R at 900, 1220, and 1227 cm^{-1} are due to the $CHCl_2$ radical[12] and the 697-cm^{-1} band is due to the HCl_2^- species.[9] The filtered photolysis studies are particularly important for grouping the new bands and characterizing the various product species. As shown in Figure 1a, photolysis with 650-1000-nm light for 60 min destroyed the 764-cm^{-1} absorption and reduced the 1194-cm^{-1} band by 0.04 absorbance units leaving a 1197, -1194-cm^{-1} doublet, which was unaffected by additional photolysis; the other absorptions in the spectrum were not changed by this photolysis. Exposure of the sample to 290-1000-nm radiation for 30 min produced changes in the spectrum which are also shown in Figure 1a and listed in Table I. Most notable were the growth of the triplet at 1045 cm^{-1} and the 1292-cm^{-1} band and the appearance of a sharp new absorption at 904.5 cm^{-1}. Additional photolysis with the full arc (220-1000 nm) reduced the latter bands and increased the yield of the free radical and HCl_2^- bands. A second study produced the same bands with similar yields and photolysis behavior. Proton radiolysis of a CH_2Cl_2 sample produced the R^+ and R bands but not the P^+ absorptions, which are also given in Table I.

$^{13}CH_2Cl_2$. Two photoionization experiments were done with 90% ^{13}C-enriched methylene chloride samples. Infrared spectra are illustrated in Figure 1b and the band positions and absorbances are listed in Table II. The most interesting new features are labeled $^{13}P^+$ at 757 and 1190 cm^{-1} and $^{13}R^+$ at 1019.8, 1016.9, 1014.2, and 1282.4 cm^{-1}. Red photolysis destroyed the 757- and 1190-cm^{-1} absorptions as shown in the dashed trace in the figure. Photolysis with 290-1000-nm light for 15 min markedly increased the $^{13}R^+$ bands and produced new 873- and 904.5-cm^{-1} absorptions. These features were increased by 30 min of 220-1000-nm photolysis which is shown in Figure 1b.

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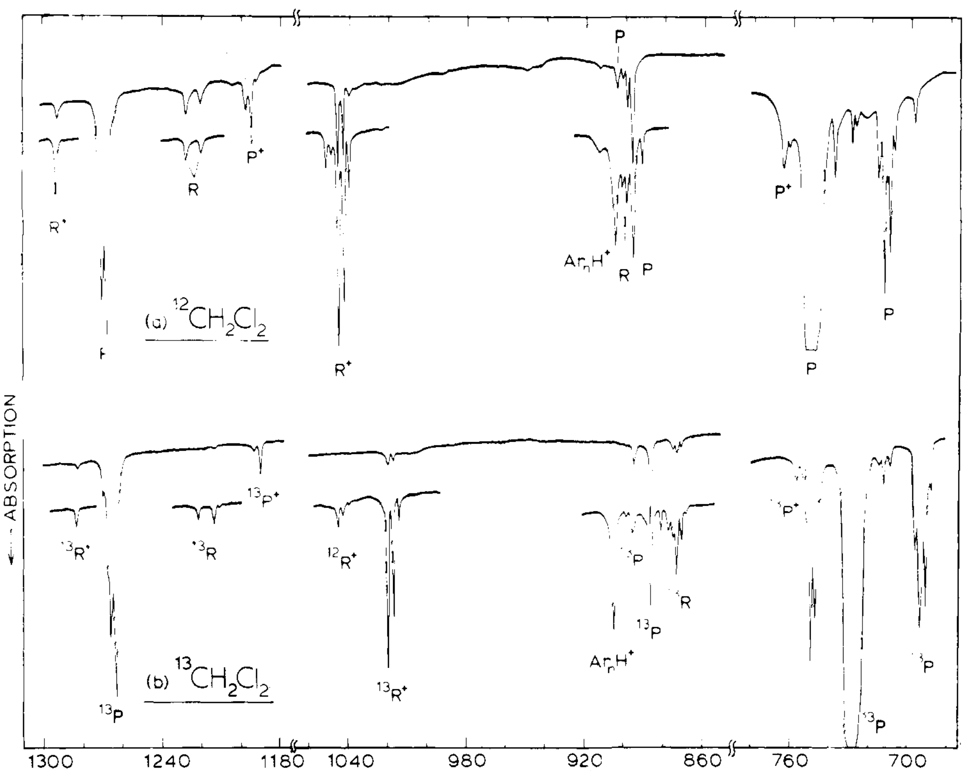

Figure 1. Infrared spectra of methylene chloride samples, $Ar/CH_2Cl_2 = 400/1$, deposited at 15 K with simultaneous exposure to argon discharge radiation. (a) CH_2Cl_2 sample. Dashed traces show changes after 60 min of 650-1000-nm photolysis; solid inset scan recorded after 30 min of 290-1000-nm photolysis. (b) $^{13}CH_2Cl_2$ sample, 90% ^{13}C enriched. Dashed traces show changes after 30 min of 650-1000-nm photolysis; solid inset scan recorded after exposure to 15 min of 290-1000-nm and 30 min of 220-1000-nm photolysis.

CD_2Cl_2. Photoionization experiments were performed with two CD_2Cl_2 samples. The infrared spectra are shown in Figure 2 and the bands are listed in Table III. The new P^+ band at 611, 605 cm^{-1} was destroyed by red photolysis. Absorptions at 465 cm^{-1} due to DCl_2^-, 644, 816, and 974 cm^{-1} due to the $CDCl_2$ radical,[12] and R^+ triplets at 863.5, 864.5, and 865.7 cm^{-1} and 1124.8, 1126.3, and 1128.0 cm^{-1} increased with the photolysis sequence given in the table. The spectrum after 220-1000-nm photolysis is shown in Figure 2. Two radiolysis experiments were performed, the first using protons and the second deuterons. Band absorbances were slightly higher in the latter case and are given in Table III; however, the 644-cm^{-1} band was tenfold more intense using deuteron bombardment. Exposing the sample to the heated light bulb filament destroyed the 605, 611 cm^{-1} bands without affecting the rest of the spectrum.

CH_2ClBr. A proton radiolysis experiment with an $Ar/CH_2ClBr = 400/1$ sample produced a strong structured absorption at 860 cm^{-1} ($A = 0.50$) and bands at 1188 and 1196 cm^{-1} ($A = 0.11$) due to the CHClBr radical,[13] a new doublet at 993, 989 cm^{-1} ($A = 0.16, 0.05$) and a weaker 1256-cm^{-1} band ($A = 0.02$). An argon photoionization experiment yielded a sharp weak 1166-cm^{-1} band ($A = 0.02$) and a weak 993-cm^{-1} absorption without any new bands in the carbon-halogen stretching region. Red photolysis destroyed the 1166-cm^{-1} feature. Pyrex-filtered photolysis produced a sharp 993.5-, 989.0-cm^{-1} doublet ($A = 0.14, 0.045$), a 1256-cm^{-1} band ($A = 0.02$), and a 904-cm^{-1} band ($A = 0.02$). Full arc photolysis halved the 989-, 993-, and 1256-cm^{-1} features, increased weak CHClBr radical bands at 861, 866, 1188, and 1196 cm^{-1}, and produced a new unidentified doublet at 1122, 1118 cm^{-1} ($A = 0.06, 0.02$).

CH_2Br_2. Methylene bromide was the subject of several studies. Photoionization produced the spectrum shown in Figure 3a and the bands listed in Table IV. The new features of most interest appeared at 685, 695, and 1129 cm^{-1}, which are labeled P^+, and at 897 and 1229 cm^{-1}, labeled R^+. New absorptions labeled R due to the $CHBr_2$ radical[13] appeared at 778, 786, and 1165 cm^{-1}; bands due to CH_2Br radical[14] at 368 and 1356 cm^{-1}, HBr_2^- at 729 cm^{-1},[1,15] and CBr_2 at 641 cm^{-1} were also observed.[16] As shown in Figure 3a, red mercury arc photolysis destroyed the 685-, 695-, and 1129-cm^{-1} bands, uncovering a residual CH_2Br absorption at 693 cm^{-1}, without altering the rest of the spectrum. Full arc photolysis slightly reduced the R^+ bands and produced a new feature at 904.5 cm^{-1}, also shown in Figure 3a. Proton radiolysis of a CH_2Br_2 sample gave more intense product bands as listed in Table IV. Sample exposure to the light-bulb filament destroyed the 685-, 695-cm^{-1} bands; the 1129-cm^{-1} region was unfortunately not rescanned after photolysis in this experiment.

CD_2Br_2. Methylene-d_2 bromide was subjected to argon resonance photoionization, and the infrared data are given in Figure 3b and Table V. New features of particular interest appeared at 547 cm^{-1} (labeled P^+) and 781 and 1015 cm^{-1} (labeled R^+) and 1020 cm^{-1}; the $CDBr_2$ radical,[13] labeled R, was also observed at 725 and 899 cm^{-1}. Red photolysis destroyed the 547-cm^{-1} feature, Pyrex photolysis increased the R^+ bands at 781 and 1014 cm^{-1} and produced a weak 644-cm^{-1} band, and full arc photolysis reduced the R^+ bands and increased the 644-cm^{-1} absorption. A proton radiolysis experiment produced a greater yield of product absorptions, as listed in Table V; light-bulb photolysis for 1 h destroyed the 547-cm^{-1} absorption, without affecting the rest of the spectrum.

CH_2I_2. One photoionization experiment was done with methylene iodide. Several weak product bands were observed; the most noteworthy are at 1165 cm^{-1} ($A = 0.03$), 805 cm^{-1} ($A = 0.06$), and 791 cm^{-1} ($A = 0.03$).

Ultraviolet Spectra. Ultraviolet absorption spectra for samples of CH_2Cl_2, CH_2Br_2, and CH_2I_2 condensed with si-

Table I. Absorption Band Positions (cm^{-1}) and Intensities (Absorbance Units) in CH_2Cl_2 Photoionization and Proton Radiolysis Experiments[a]

abs	I_0	$h\nu_1$	$h\nu_2$	$h\nu_3$	rad	assign
396	0.03	0.03	0.04	0.05	0.14	CH_2Cl
697	0.06	0.06	0.08	0.10	0.15	HCl_2^-
764	0.05	0.0	0.0	0.0	0.0	$CH_2Cl_2^+$
898	0.07	0.07	0.14	0.15		$CHCl_2$
900	0.03	0.03	0.08	0.10	0.10	$CHCl_2$
904.5	0.0	0.0	0.16	0.06	0.0	Ar_nH^+
1039.8	0.02	0.02	0.08	0.05	0.03	$CH^{37}Cl_2^+$
1042.5	0.12	0.12	0.37	0.25	0.11	$CH^{35}Cl^{37}Cl^+$
1045.4	0.17	0.17	0.55	0.36	0.17	$CH^{35}Cl_2^+$
1049	0.0	0.0	0.03	0.0	0.0	site
1052	0.0	0.0	0.05	0.0	0.0	site
1194	0.06	0.02[b]	0.02	0.02	0.0	$CH_2Cl_2^+$
1197	0.03	0.03	0.03	0.03	0.0	product
1220	0.03	0.03	0.02	0.04	0.07	$CHCl_2$
1227	0.04	0.04	0.03	0.05	0.07	$CHCl_2$
1292.0	0.03	0.03	0.10	0.07	0.03	$CHCl_2^+$
2477	0.04	0.04	0.02			HB[c]
2767	0.08	0.08	0.08	0.07		?
2886	0.18	0.18	0.18	0.16		?
2998	0.22	0.22	0.22	0.22		CH_2Cl_2

[a] Filtered high-pressure mercury-arc wavelengths used in photoionization study: $h\nu_1$ is 60 min of 650-1000 nm photolysis, $h\nu_2$ is 30 min of 290-1000 nm, and $h\nu_3$ is 45 min of 220-1000 nm photolysis. [b] Residual absorption associated with 1197-cm^{-1} product band which is tentatively assigned to CCl_2^+. [c] Tentatively assigned to the H-Cl stretching mode of an intramolecular hydrogen-bonded anion of the form Cl-H- - -$(CHCl)^-$.

Table II. Absorption Band Positions (cm^{-1}) and Intensities (Absorbance Units) in the $^{13}CH_2Cl_2$ (90% ^{13}C) Photoionization Experiment[a]

abs	I_0	$h\nu_1$	$h\nu_2$	$h\nu_3$	assign
393	0.02	0.02	0.02		$^{13}CH_2Cl$
757	0.02	0.0	0.0	0.0	$^{13}CH_2Cl_2^+$
868.0	0.00	0.00	0.0	0.01	$^{13}CH^{37}Cl_2$
870.5	0.010	0.010	0.03	0.04	$^{13}CH^{35}Cl^{37}Cl$
873.0	0.015	0.015	0.04	0.07	$^{13}CH^{35}Cl_2$
904.5	0.0	0.0	0.07	0.18	Ar_nH^+
1014.2	0.00	0.00	0.025	0.03	$^{13}CH^{37}Cl_2^+$
1016.9	0.010	0.010	0.15	0.18	$^{13}CH^{35}Cl^{37}Cl^+$
1019.8	0.015	0.015	0.24	0.28	$^{13}CH^{35}Cl_2^+$
1023	0.00	0.00	0.01	0.00	site
1026	0.00	0.00	0.02	0.00	site
1042	0.00	0.00	0.00	0.02	$^{12}CH^{35}Cl^{37}Cl^+$
1045	0.00	0.00	0.00	0.03	$^{12}CH^{35}Cl_2^+$
1190	0.05	0.00	0.00	0.00	$^{13}CH_2Cl_2^+$
1214	0.00	0.00	0.01	0.03	$^{13}CHCl_2$
1221	0.00	0.00	0.00	0.02	$^{13}CHCl_2$
1282.4	0.00	0.00	0.02	0.025	$^{13}CHCl_2^+$
2476	0.04				HB
2762	0.06	0.06	0.06	0.05	?
2879	0.16	0.16	0.16	0.14	?
2991	0.09	0.09	0.09	0.08	$^{13}CH_2Cl_2$

[a] Filtered mercury-arc photolysis: $h\nu_1$ is 30 min of 650-1000 nm, $h\nu_2$ is 15 min of 290-1000 nm, and $h\nu_3$ is 30 min of 220-1000 nm photolysis.

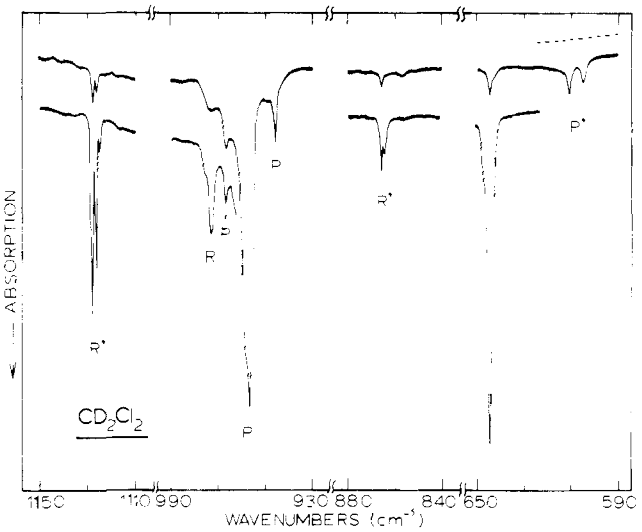

Figure 2. Infrared spectra of methylene-d_2 chloride, Ar/CD_2Cl_2 = 400/1, deposited at 15 K during exposure to argon resonance radiation. The dashed trace shows changes after 30 min of 650-1000-nm photolysis. The bottom scan was recorded after exposure of the sample to 340-1000, 290-1000, and 220-1000 nm radiation for 35-min periods.

Table III. Absorption Band Positions (cm^{-1}) and Intensities (Absorbance Units) in CD_2Cl_2 Photoionization and Deuteron Radiolysis Experiments[a]

abs	I_0	$h\nu_1$	$h\nu_2$	$h\nu_3$	$h\nu_4$	rad	assign
465	0.01	0.01	0.01	0.01	0.03	0.31	DCl_2^-
605	0.02	0.00	0.00	0.00	0.00	0.06	$CD_2Cl_2^+$
611	0.05	0.00	0.00	0.00	0.00	0.11	$CD_2Cl_2^+$
644	0.04	0.04	0.05	0.62	1.2	2	Ar_nD^+
747	0.12	0.12	0.12	0.12	0.12	0.62	CCl_2
755	0.03	0.03	0.03	0.03	0.02	0.0	?
761	0.09	0.09	0.09	0.09	0.07	0.0	?
816	0.00	0.00	0.00	0.00	0.02	0.05	$CDCl_2$
864.5	0.01	0.01	0.01	0.04	0.04	0.0	$CD^{35}Cl^{37}Cl^+$
865.7	0.02	0.02	0.02	0.07	0.07	0.0	$CD^{35}Cl_2^+$
974	0.03	0.03	0.03	0.03	0.10	0.28	$CDCl_2$
1124.8	0.00	0.00	0.00	0.03	0.03	0.0	$CD^{37}Cl_2^+$
1226.3	0.03	0.03	0.03	0.19	0.18	0.0	$CD^{35}Cl^{37}Cl^+$
1128.0	0.05	0.05	0.05	0.28	0.27	0.0	$CD^{35}Cl_2^+$
1194	0.04	0.04	0.04	0.04	0.04	0.00	product
1197	0.06	0.06	0.06	0.06	0.06	0.00	product
1818	0.06	0.06	0.06	0.03	0.00		HB
2037	0.09	0.09	0.09	0.08	0.07		?
2132	0.12	0.12	0.12	0.10	0.08		?
2205	0.26	0.26	0.26	0.26	0.23		CD_2Cl_2

[a] Filtered mercury arc photolysis wavelengths used in photoionization study: $h\nu_1$ is 30 min of 650-1000 nm, $h\nu_2$ is 35 min of 340-600 nm, $h\nu_3$ is 35 min of 290-1000 nm, and $h\nu_4$ is 40 min of 220-1000 nm photolysis.

multaneous exposure to intense argon resonance radiation are contrasted in Figure 4. The new product absorption bands shifted to the red with increasing halogen size. The spectrum of 2 mmol of an Ar/CH_2I_2 = 400/1 sample revealed two weak absorptions at 245 and 285 nm (A = 0.02 and 0.09, respectively) due to CH_2I_2; photoionization of 2 additional mmol of sample during deposition for 1 h produced the spectrum shown in Figure 4c. Notice the strong absorption at 375 nm (A = 0.28) and the two weak relatively broad bands at 465 and 555 nm. The sample was photolyzed with 650-1000-nm high-pressure mercury arc light for 30 min using a 45° ultraviolet mirror to direct the radiation; the 375 and 555 nm absorptions were reduced to half of their initial absorbance above the background, while the 465-nm band increased to 150% and the 285- and 245-nm bands remained unchanged. A similar photolysis with 500-1000-nm light reduced the 375- and 555-nm bands to 25% of their original intensity, increased the 465-nm band to 200%, and left the CH_2I_2 bands unchanged; the spectrum following this irradiation is shown displaced in Figure 4c. Additional photolysis with 290-1000-nm light further reduced the 375- and 555-nm bands slightly, but the CH_2I_2 bands also decreased by 20% suggesting competing photolysis reactions.

The ultraviolet spectrum of 2 mmol of Ar/CH_2Br_2 = 400/1

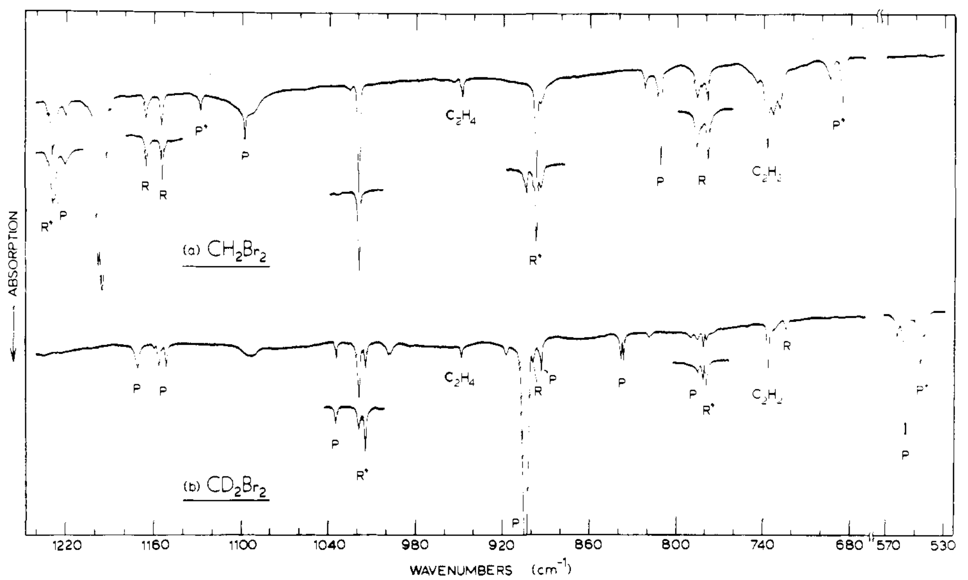

Figure 3. Infrared spectra of methylene bromide samples, Ar/CH_2Br_2 = 400/1, deposited at 15 K with simultaneous exposure to argon discharge radiation. (a) CH_2Br_2 sample. Dashed traces show changes after 30 min of 650-1000-nm photolysis; solid inset scan recorded after 30 min of 220-1000-nm photolysis. (b) CD_2Br_2 sample. Dashed trace shows change after 30 min of 650-1000-nm photolysis; solid inset scan recorded after 30 min of 290-1000-nm photolysis.

Table IV. Absorption Band Positions (cm^{-1}) and Intensities (Absorbance Units) in CH_2Br_2 Photoionization and Proton Radiolysis Experiments[a]

abs	I_0	$h\nu_1$	$h\nu_2$	rad	assign
368	0.05	0.05	0.05	0.00	CH_2Br
641	0.40	0.40	0.40	?	CBr_2
685	0.10	0.00	0.00	0.15	$CH_2Br_2^+$
695	0.04	*b*	*b*	0.25	$CH_2Br_2^+$
729	0.08	0.08	0.08	0.10	HBr_2^-
737	0.20	0.20	0.20	0.15	C_2H_2
778	0.08	0.08	0.10	0.60	$CHBr_2$
786	0.06	0.06	0.08	0.50	$CHBr_2$
897	0.28	0.28	0.19	0.30	$CHBr_2^+$
904.5	0.00	0.00	0.03	0.00	Ar_nH^+
1020	0.30	0.30	0.16	0.00	product
1129	0.03	0.00	0.00	0.00	$CH_2Br_2^+$
1155	0.06	0.06	0.08	0.16	$CHBr_2$
1165	0.06	0.06	0.06	0.15	$CHBr_2$
1229	0.05	0.05	0.03	0.05	$CHBr_2^+$
1356	0.02	0.02	0.02	0.02	CH_2Br
2901	0.23	0.23	0.00		HB[c]
3011	0.05	0.05	0.05		CH_2Br_2

[a] Filtered photolysis for photoionization study: $h\nu_1$ is 30 min of 650-1000 nm and $h\nu_2$ is 30 min of 220-1000 nm photolysis. [b] Residual 693-cm^{-1} band due to CH_2Br. [c] Tentatively assigned to the hydrogen-bonded C-H stretching mode of an intramolecular hydrogen-bonded anion of the form Br^-- -HCHBr.

sample exhibited a weak absorption at 270 nm; photoionization of 3 additional mmol of sample during deposition gave the spectrum illustrated in Figure 4b. A pronounced shoulder was found at 270 nm, a strong absorption was observed at 362 nm (A = 0.40), and a weak broad band was found in the visible region at 545 nm. Photolysis with 650-1000-nm light for 30 min reduced the 362- and 545-nm absorptions to one-quarter of their original intensity; exposure to 500-1000-nm radiation for 30 min further reduced the 362-nm band to A = 0.03 and the weak 545-nm band was similarly reduced, as is shown in the displaced trace in Figure 4b. A final 290-1000-nm photolysis reduced the 362-nm band to A = 0.01 revealing a weak 300-nm absorption in the sample. Another CH_2Br_2 experiment was performed photoionizing a total of 6 mmol of sample. The 362-nm band was increased to A = 0.75 and the 545-nm absorption to A = 0.03. This sample revealed no absorptions out to 2600 nm, which overlapped with the infrared spectrum. A 30-min photolysis with 500-1000-nm light reduced the 362-nm band to A = 0.09.

Two similar experiments were conducted with methylene chloride and the optical spectrum is shown in Figure 4a. A new medium-intensity absorption was observed at 342 nm (A = 0.15). Exposure of this sample to 650-1000-nm radiation for 30 min reduced the 342-nm absorption to A = 0.09, and the spectrum recorded after 500-1000-nm photolysis, shown displaced in Figure 4a, revealed a further substantial reduction in the 342-nm band (A = 0.02).

One photoionization experiment was done with CH_2ClBr and the spectrum contour was similar to the CH_2Cl_2 trace in Figure 4a; the band center appeared at 340 nm. Red photolysis reduced the band area by one-third, and yellow photolysis reduced it to 40% of the original band area.

Discussion

The new species produced in these experiments will be identified and their mechanism of formation and photolysis will be discussed.

Parent Cations. The electronic structure of the CH_2X_2 molecules can be written $(a_1)^2(b_1)^2(a_1)^2(b_2)^2[(a_1)^2(a_2)^2(b_1)^2(b_2)^2]$. Of particular interest here, the (b_2) orbital is C-X bonding and the orbitals in brackets are generated from halogen lone-pair p orbitals. The ground state $CH_2X_2^+$ ion is probably formed by removal of a $[(b_1)]$ or $[(b_2)]$ electron corresponding to the lowest energy photoelectron band appearing at 11.3 eV. Photoelectron bands in the 13-16-eV region probably correspond to removal of the (a_1), (b_1), and (b_2) bonding electrons.[3]

The ultraviolet absorption spectra for matrix samples of CH_2Cl_2, CH_2Br_2, and CH_2I_2 exposed to ionizing radiation during condensation reveal major bands at 342, 362, and 375 nm, respectively, which are shown in Figure 4. These absorptions were reduced substantially by 650-1000-nm light and essentially destroyed by 500-1000-nm radiation; this indicates that the absorbing species is quite photosensitive. Furthermore, the presence of a visible absorption for the ultraviolet absorbing species is demonstrated by this photodestruction and by broad bands centered at 545 nm in the CH_2Br_2 study and at 555 nm in the CH_2I_2 experiment.

Table V. Absorption Band Positions (cm^{-1}) and Intensities (Absorbance Units) in CD_2Br_2 Photoionization and Proton Radiolysis Experiments[a]

abs	I_0	$h\nu_1$	$h\nu_2$	$h\nu_3$	rad	assign
363	0.03	0.03	0.03	0.03	0.0	CD_2Br
498	0.07	0.07	0.07	0.10	0.10	DBr_2^-
547	0.11	0.00	0.00	0.00	0.18	$CD_2Br_2^+$
641	0.26	0.26	0.14	0.10	2	CBr_2
644	0.00	0.00	0.02	0.11	*b*	Ar_nD^+
725	0.01	0.01	0.01	0.01	0.15	$CDBr_2$
781	0.01	0.01	0.04	0.02	0.10	$CDBr_2^+$
899	0.02	0.02	0.02	0.02	0.25	$CDBr_2$
1015	0.04	0.05	0.08	0.05	0.03	$CDBr_2^+$
1016	0.04	0.04	0.04	0.04	*b*	CD_2Br
1020	0.12	0.08	0.04	0.02		product
2130	0.16	0.16	0.04	0.00		HB
2208	0.09	0.09	0.09	0.09		CD_2Br_2

[a] Filtered photolysis for photoionization study: $h\nu_1$ is 30 min of 650–1000 nm, $h\nu_2$ is 30 min of 290–1000 nm, and $h\nu_3$ is 30 min of 220–1000 nm photolysis. [b] Not resolved from adjacent absorption.

The near-UV absorptions at 342, 362, and 375 nm are assigned to transitions of the parent ions $CH_2Cl_2^+$, $CH_2Br_2^+$, and $CH_2I_2^+$; the upper state corresponds to the same excited state reached by the 15.2, 14.1, and 12.8 eV photoelectron bands[3] of the methylene halides, respectively. The transition from the parent ion ground state to this excited state can be calculated from the photoelectron spectrum as the difference between the ionization energies of this excited state and the ground ionic state. The calculated absorption band positions are 320, 357, and 379 nm, respectively, for $CH_2Cl_2^+$, $CH_2Br_2^+$, and $CH_2I_2^+$, as compared to the observed absorption band centers of 342, 362, and 375 nm. The small differences probably arise from slightly different Franck-Condon factors for the two ionization transitions and the observed electronic transition of the ion. This agreement between the matrix absorption and gaseous photoelectron spectra provides strong support for the matrix spectroscopic observation of the methylene halide parent ions.

The ultraviolet electronic transition for each of the parent cations probably involves promotion of an electron from a C-X bonding orbital (probably (b_2))[3] to the hole in the mostly nonbonding halogen lone-pair orbital of the ground state ion. Since the ultraviolet absorptions were destroyed by visible radiation, this excited state is apparently repulsive, dissociating to CH_2X^+ and X.

The new infrared absorptions labeled P^+ are grouped by their sensitivity to visible radiation, which is consistent with their assignment to the parent ions $CH_2X_2^+$. Three sharp infrared bands in the 1100-cm^{-1} region, 1194 cm^{-1} for CH_2Cl_2, 1166 cm^{-1} for CH_2ClBr, and 1129 cm^{-1} for CH_2Br_2, demonstrate a dependence on two halogens since only three new bands were observed. These new bands are respectively 73, 65, and 66 cm^{-1} *below* the strong ν_8 (b_2) hydrogen wagging mode of the corresponding neutral parent molecule. This single sharp $^{13}P^+$ band at 1190 cm^{-1} exhibits a 4-cm^{-1} ^{13}C shift, the same as the ν_8 parent band, and shows that this absorber contains a single carbon atom. The 1194-, 1166-, and 1129-cm^{-1} bands are assigned to ν_8 of the parent ions. The deuterium counterparts of these bands were unfortunately too weak to be observed. In the carbon–halogen stretching region, the P^+ bands were observed above the ν_9 (b_2) antisymmetric C–X_2 modes for the parent hydrogen compounds and below the ν_9 modes for the parent deuterium precursors, which are compared in Table VI. Halogen stretching modes were not observed for CH_2ClBr^+ owing possibly to low intensity or masking by the parent.

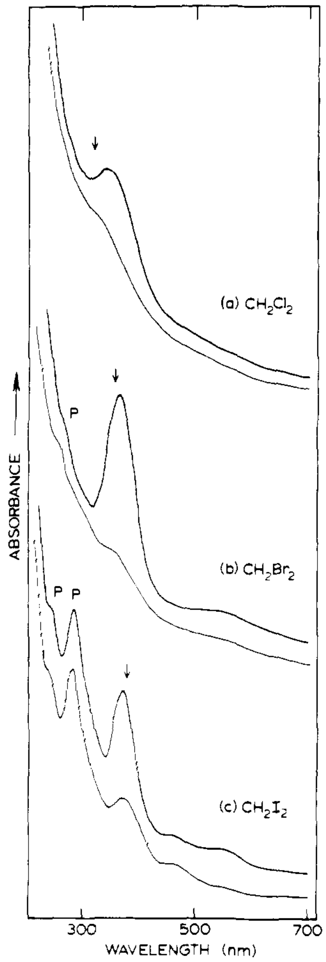

Figure 4. Absorption spectra from 200–700-nm for methylene halide samples, Ar/CH_2X_2 = 400/1, deposited at 20 K with simultaneous exposure to argon discharge radiation: (a) CH_2Cl_2, (b) CH_2Br_2, (c) CH_2I_2. The trace displaced below each scan was recorded after successive 30 min of 650–1000-nm *and* 500–1000-nm photolysis periods. The arrows denote the position of transitions from the ground state of the ions to the excited state of the ions determined from the photoelectron spectra in ref 3.

Table VI. Antisymmetric (b_2) Vibrational Mode Frequencies (cm^{-1}) for the Methylene Chloride and Bromide Neutrals and Cations in Solid Argon

	ν_8 (CH_2 wag)[a]	ν_9 (C–Cl_2 str)
CH_2Cl_2	1267	747
$CH_2Cl_2^+$	1194	764
$^{13}CH_2Cl_2$	1263	729
$^{13}CH_2Cl_2^+$	1190	757
CD_2Cl_2	957	723
$CD_2Cl_2^+$		611
CH_2Br_2	1195	650
$CH_2Br_2^+$	1129	695
CD_2Br_2	905	621
$CD_2Br_2^+$		547

[a] Analogous data for the CH_2 wag of CH_2ClBr and CH_2ClBr^+ are 1231 and 1166 cm^{-1}, respectively.

The first photoelectron band for $CH_2Cl_2^+$ shows three vibrational peaks with spacings of 650 cm^{-1} which have been attributed to the symmetric C–Cl_2 stretching frequency of the ion;[3] this observation is compatible with the present 764-cm^{-1} measurement of the antisymmetric C–Cl_2 stretching mode of $CH_2Cl_2^+$.

The ratio of the ν_9 modes for CH_2Cl_2 and CH_2Br_2, 1.15, is a quantitative measure of the carbon–halogen stretching character of this vibration; this ratio for the analogous P^+ bands is 1.10. Similarly, the ν_9 ratio for the deuterated neutrals is 1.17 and the P^+ band ratio is 1.12. These ratios indicate mode mixing with another vibration in the ion, which is confirmed by the isotopic shifts. The ^{13}C shift from 764 to 757 cm^{-1} for the ion is considerably less than the parent compound ^{13}C shift from 749 to 728 cm^{-1}, while the deuterium shift of 764 to 611 cm^{-1} for the ion is considerably more than the analogous parent shift of 749 to 723 cm^{-1}. All of the above facts indicate that the lower frequency set of P^+ bands are due to a mixed hydrogen rocking carbon-halogen stretching vibration of the parent cation. In the $CD_2Cl_2^+$ and $CH_2Br_2^+$ cases, this band is site split by the matrix.

A possible explanation for the unusual isotopic frequency shifts and mode mixing in the parent cations involves electronic state considerations. Theoretical calculations predict that the ground state of $CH_2Cl_2^+$ is formed by removal of a $[(b_1)]$ electron, while the state produced by ionization of a $[(b_2)]$ electron lies only slightly higher in energy.[17] The $CH_2Cl_2^+$ photoelectron spectrum shows two strong peaks in the lowest energy region which have been assigned to removal of electrons from the four halogen molecular orbitals, with each photoelectron peak assigned to two overlapping bands.[3] Hence, the ground state of the ion has an excited state quite close in energy. When spin-orbit coupling of the electron spin on the ionized chlorine in the parent cation is taken into account, these two electronic states have the same spin-orbit representation, $E_{1/2}$, and they can strongly interact. This electronic interaction through spin-orbit mixing can shift the electronic energy levels and/or change the vibrational potential function for the ion.[18] A similar spin-orbit interaction in CH_3Cl^+ has distorted the lower vibrational levels of the ground state of the ion, as seen in the first photoelectron band of CH_3Cl^+.[3]

Daughter Ions. The triplet at 1045.4, 1042.5, and 1039.8 cm^{-1} in CH_2Cl_2 experiments exhibits the appropriate relative intensities for isotopic splittings of two equivalent chlorine atoms in natural abundance. The ^{13}C shifted triplet at 1019.8 1016.9, and 1014.2 cm^{-1} exhibits identical 2.8 ± 0.1 cm^{-1} chlorine isotopic splittings. The relative intensities of the ^{13}C and ^{12}C bands in the 90% ^{13}C enriched CH_2Cl_2 experiment confirm the presence of a single carbon atom in this new R^+ species. The isotopic data dictate assignment of this R^+ band to the antisymmetric C–Cl vibration of $CHCl_2^+$. This triplet is 7 cm^{-1} higher than the triplet observed in chloroform work[7,8] which has been recently shown to be due to $(CHCl_2^+)Cl$, i.e., the $CHCl_2^+$ cation with the other chlorine atom from the $CHCl_3$ precursor trapped in the same matrix cage.[8] The hydrogen deformation mode of the isolated cation at 1292.0 cm^{-1} is 1 cm^{-1} above this mode for $(CHCl_2^+)Cl$ as is the case for the ^{13}C counterpart at 1282.4 cm^{-1}.

In the deuterium species, the deformation is displaced into the region of the antisymmetric $C-Cl_2$ stretching vibration and considerable mode mixing results, which is illustrated by the triplet chlorine isotopic splittings for each deuterium R^+ band. The present $CDCl_2^+$ bands are also slightly higher in frequency than their analogues produced from $CDCl_3$, owing to the extra chlorine from the latter precursor being trapped with the daughter cation.

A similar case can be made for the R^+ bands in CH_2ClBr, CH_2Br_2, and CD_2Br_2 experiments. The assignments are summarized in Table VII where the present CHX_2^+ modes are contrasted with the $(CHX_2^+)X$ species from haloform experiments[8] and the CHX_2 radical vibrations. It is seen that the presence of another halogen atom in the matrix cage displaces the $C-X_2$ modes 1 to 13 cm^{-1} from the isolated ion values.

Of more chemical interest is the radical-cation comparison. Substantial increases in both $C-X_2$ stretching and H–C–X deformation frequencies are found upon ionization. Since the free-radical electron is antibonding in a $C-X_2$ molecular orbital system involving p- orbitals, its removal will strengthen the C–X bonds and increase the $C-X_2$ vibrational frequency, as found experimentally.

The weak bands at 1165 and 805 cm^{-1} in the CH_2I_2 experiment are tentatively assigned to the antisymmetric deformation and $C-I_2$ stretching modes, respectively, of CHI_2^+. These values correlate nicely with the halogen trend in Table VII and the analogous frequencies for CHI_2 radical.[19]

Ar_nD^+ and Ar_nH^+. The sharp 644-cm^{-1} absorption which appeared on photolysis in CD_2Cl_2 and CD_2Br_2 experiments is due to Ar_nD^+.[9,20] The 644-cm^{-1} band increased from A = 0.04 to 1.2 on full arc photolysis in the CD_2Cl_2 experiment. It is noteworthy that H^+ bombardment of CD_2Cl_2 samples produced the 644-cm^{-1} band (A = 0.20), but D^+ radiolysis gave an increased 644-cm^{-1} band yield ($A > 2$). The hydrogen counterpart, produced on photolysis in all of these CH_2X_2 experiments at 904.5 cm^{-1}, is the Ar_nH^+ species.

Mechanism of Formation. A substantial amount of evidence has shown that the open argon discharge tube functions as a photoionization source in these experiments.[1,8,9,21] Since the ionization potentials of CH_2Cl_2 and CH_2Br_2, 11.32 and 10.52 eV,[4,5] are easily reached by the intense argon resonance lines at 11.6 and 11.8 eV, it is proposed that the parent ions are produced by direct photoionization, reactions 1 and 2, during matrix sample condensation.

$$CH_2Cl_2 + h\nu\ (11.6\text{-}11.8\ \text{eV}) \rightarrow CH_2Cl_2^+ + e^- \quad (1)$$

$$CH_2Br_2 + h\nu\ (11.6\text{-}11.8\ \text{eV}) \rightarrow CH_2Br_2^+ + e^- \quad (2)$$

The daughter radical arises from precursor photodissociation, reaction 3. Ionization energies of these radicals are 9.5–8.1 eV,[22]

$$CH_2X_2 + h\nu\ (11.6\text{-}11.8\ \text{eV}) \rightarrow CHX_2 + H \quad (3)$$

and they can be ionized by a second vacuum-ultraviolet photon,

$$CHX_2 + h\nu\ (11.6\text{-}11.8\ \text{eV}) \rightarrow CHX_2^+ + e^- \quad (4)$$

Mechanism of Photolysis. Selective photolysis of the matrix samples formed by precursor photoionization is important to characterize the new ion products and their photochemistry. The appearance potential of CH_2Cl^+ from CH_2Cl_2, 12.14 eV, and the ionization potential of CH_2Cl_2, 11.32 eV,[4] give the threshold energy for dissociation of $CH_2Cl_2^+$, reaction 5, as 0.82 eV.

$$CH_2Cl_2^+ + h\nu\ (650\text{-}1000\ \text{nm}) \rightarrow CH_2Cl^+ + Cl \quad (5)$$

Although the absorption maximum for $CH_2Cl_2^+$ appears in the ultraviolet at 342 nm, this ion absorbs continuously and photodissociates in the visible; analogous arguments hold for $CH_2Br_2^+$. Both of these parent ions are in fact extremely facile in the gas phase; they undergo collisional dissociation with endoergicities of 0.7–0.8 eV.[4,6] The extreme photosensitivity of these parent cations explains the failure to observe $CH_2Cl_2^+$ in the proton beam experiment and the need to use a far-infrared transmitting filter to prevent near-infrared source light from destroying these species while infrared spectra were recorded.

No new infrared absorptions appeared in the spectra after 650–1000-nm photolysis; apparently, the CH_2X^+ product was not formed in detectable quantity. However, photolysis with near-ultraviolet light caused further reaction of the CH_2X^+ and X photoproducts of reaction 5, which must be trapped in the same matrix cage.

$$(CH_2X^+)X + h\nu\ (290\text{-}1000\ \text{nm}) \rightarrow CHX_2^+ + H \quad (6)$$

$$(CH_2X^+)X + n\text{Ar} + h\nu\ (220\text{-}1000\ \text{nm}) \rightarrow CHX_2 + Ar_nH^+ \quad (7)$$

Table VII. Comparison of Antisymmetric Vibrational Frequencies (cm^{-1}) for CHX_2 Species

$CHCl_2^+$	$(CHCl_2^+)Cl$	$CHCl_2$	$CDCl_2^+$	$(CDCl_2^+)Cl$	$CDCl_2$
1045	1038	902	866	864	816
1292	1291	1226	1128	1122	974
$CHClBr^+$	$(CHClBr^+)$-Br^a	$CHClBr$			
993	997	866			
1256	1256	1186			
$CHBr_2^+$	$(CHBr_2^+)Br$	$CHBr_2$	$CDBr_2^+$	$(CDBr_2^+)Br$	$CDBr_2$
897	900	786	781	768	725
1229	1226	1165	1015	1008	899
CHI_2^+		CHI_2			
805		717			
1165		1112			

[a] For comparison, $(CHClBr^+)Cl$ absorbs at 988 and 1254 cm^{-1} ref 8.

The daughter cation absorptions significantly increased with Pyrex-filtered photolysis reaction 6; the bands produced by photolysis were identical in position to the original photoionization product, which is assigned here to the isolated CHX_2^+ ion. With continued full arc photolysis, the radical CHX_2 and Ar_nH^+ absorptions increased (reaction 7), and the CHX_2^+ absorptions decreased in all of the present experiments. Photodetachment of electrons from halide ions, formed in the matrix photoionization process, is accessible with this energy radiation,[23] and neutralization of some CHX_2^+ could also result in the growth of CHX_2 radical,

$$CHX_2^+ + X^- + h\nu\ (220\text{-}1000\ \text{nm}) \rightarrow CHX_2 + X \quad (8)$$

Further evidence for the trapping of the original halogen atom from the precursor molecule in the same matrix cage in reaction 5, and for the mechanisms 6 and 7, comes from the CH_2ClBr experiments. Mercury arc photolysis produced growth of $CHClBr^+$ and $CHClBr$ radical with no $CHCl_2^+$, $CHCl_2$, $CHBr_2^+$, or $CHBr_2$ being formed. Analogous behavior was found in the earlier haloform experiments: photolysis gave marked growth of CX_3^+ and CX_3 absorptions, and with mixed chlorobromo precursors, no halogen scrambling was found.[8]

Conclusions

Matrix photoionization of CH_2Cl_2 and CH_2Br_2 produced and trapped the $CH_2X_2^+$ and CHX_2^+ ions in solid argon for spectroscopic and photochemical study. The antisymmetric vibrations observed for the parent ions show unusual mode mixing, which is explained by spin-orbit interaction of the lowest two electronic states of $CH_2X_2^+$ with some distortion of the vibrational potential function. The ions $CH_2Cl_2^+$ and $CH_2Br_2^+$ photodissociated with red-visible light, which is consistent with their matrix electronic absorption spectra and their limited stability in the gas phase. Ultraviolet photolysis of these matrix samples produced the isolated CHX_2^+ ions, CHX_2 radicals, and the matrix solvated proton Ar_nH^+, which shows that the parent ion photolysis products were retained in the original matrix cage. The ultraviolet absorption spectrum for each parent ion corresponds to transitions to excited electronic ionic states observed in photoelectron spectra.

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References and Notes

(1) F. T. Prochaska and L. Andrews, *J. Chem. Phys.*, **67,** 1091 (1977).
(2) F. T. Prochaska and L. Andrews, *J. Am. Chem. Soc.*, **100,** 2102 (1978).
(3) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, New York, N.Y., 1970.
(4) A. S. Werner, B. P. Tasi, and T. Baer, *J. Chem. Phys.*, **60,** 3650 (1974).
(5) B. P. Tasi, T. Baer, A. S. Werner, and S. F. Lin, *J. Phys. Chem.*, **79,** 570 (1975).
(6) T. Baer, L. Squires, and A. S. Werner, *Chem. Phys. Lett.*, **6,** 325 (1974).
(7) M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **54,** 3935 (1971); M. E. Jacox, *Chem. Phys.*, **12,** 51 (1976).
(8) L. Andrews, C. A. Wight, F. T. Prochaska, S. A. McDonald, and B. S. Ault, *J. Mol. Spectrosc.*, **73,** 120 (1978).
(9) C. A. Wight, B. S. Ault, and L. Andrews, *J. Chem. Phys.*, **65,** 1244 (1976).
(10) L. Andrews, J. M. Grzybowski, and R. O. Allen, *J. Phys. Chem.*, **79**, 904 (1975).
(11) L. Andrews, *J. Chem. Phys.*, **63,** 4465 (1975).
(12) T. G. Carver and L. Andrews, *J. Chem. Phys.*, **50,** 4235 (1969).
(13) T. G. Carver and L. Andrews, *J. Chem. Phys.*, **50,** 4223 (1969).
(14) D. W. Smith and L. Andrews, *J. Chem. Phys.*, **55,** 5295 (1971).
(15) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **55,** 2550 (1971).
(16) L. Andrews and T. G. Carver, *J. Chem. Phys.*, **49,** 896 (1968).
(17) F. Hopfgarten and R. Manne, *J. Electron Spectrosc. Relat. Phenom.*, **2,** 13 (1973).
(18) G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966.
(19) D. W. Smith and L. Andrews, *J. Phys. Chem.*, **76,** 2718 (1972).
(20) M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, **46,** 460 (1973).
(21) L. Andrews, D. E. Tevault, and R. R. Smardzewski, *Appl. Spectrosc.*, **32,** 157 (1978).
(22) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. No. 1,* **6** (1977).
(23) R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38,** 1540 (1963).