Infrared Spectra of Chlorinated Ethylene Cations: $C_2Cl_4^+$, $C_2HCl_3^+$, 1,1-$C_2H_2Cl_2^+$, and *trans*-$C_2H_2Cl_2^+$ in Solid Argon

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Infrared spectra of chlorinated ethylene cations: $C_2Cl_4^+$, $C_2HCl_3^+$, 1,1-$C_2H_2Cl_2^+$, and *trans*-$C_2H_2Cl_2^+$ isolated in solid argon are presented. These cations were produced by co-deposition of chlorinated ethylene/Ar mixtures with high-frequency-discharged Ar at 4 K. Photosensitive absorptions are assigned to different vibrational modes of the cations on the basis of observed chlorine isotopic shifts and quantum chemical frequency calculations. With the removal of one electron from the HOMO of chlorinated ethylene neutrals that is C═C bonding and C−Cl antibonding in character, the observed C−Cl stretching vibrational frequencies of the cations are blue-shifted relative to those of the chlorinated ethylene neutrals. The results also show that the cations can be regarded as "isolated" with the vibrational frequencies only slightly shifted when compared to the available gas-phase values.

Introduction

As chlorinated ethylenes are widely used as solvents, these toxic compounds are widely dispersed in the atmosphere.[1] The radical cations and anions are potential important species in the processes of degradation and oxidation of chlorinated ethylenes.[2,3] Numerous experimental[4−16] and theoretical[17−19] studies have been performed on the spectra, structures, and reactions of chlorinated ethylene cations. The ionization potentials of the C_2Cl_4, C_2HCl_3, 1,1-$C_2H_2Cl_2$, *trans*-$C_2H_2Cl_2$, *cis*-$C_2H_2Cl_2$, and C_2H_3Cl were measured by earlier photoelectron spectroscopic studies.[4−7] Several vibrational fundamentals such as C−C and C−Cl stretching modes were determined.[4−7] The structures and vibrational frequencies of low-lying electronic states of the tetrachloroethylene and dichloroethylene cations were studied by ab initio calculations.[17−19] More recently, the chlorinated ethylenes C_2HCl_3 and *cis*- and *trans*-$C_2H_2Cl_2$ have been studied by employing the vacuum ultraviolet−infrared−photoinduced Rydberg ionization (VUV−IR−PIRI) spectroscopy, vacuum ultraviolet−pulsed field ionization−photoelectron (VUV−PFI−PE) spectroscopy, and one-photon mass-analyzed threshold ionization spectroscopy.[8−13] More accurate ionization potentials of the chlorinated ethylene neutrals were measured, and the vibrational frequencies of the chlorinated ethylene cations were determined.

Matrix isolation combined with laser ablation, vacuum ultraviolet photolysis, and high-frequency discharge provides a powerful method for trapping molecular ions for spectroscopic study.[20−22] Molecular ions trapped in solid noble gas matrixes often show considerably larger matrix shifts for vibrations than those of neutral species.[23] The vibrational shifts of matrix isolated cations with respect to the gas-phase values provide useful information in understanding the cation−noble gas interactions. However, only very few comparisons are possible for molecular cations observed both in the gas phase and trapped in solid argon matrix. Here, we report an infrared absorption spectroscopic study of the chlorinated ethylene cations in solid argon.

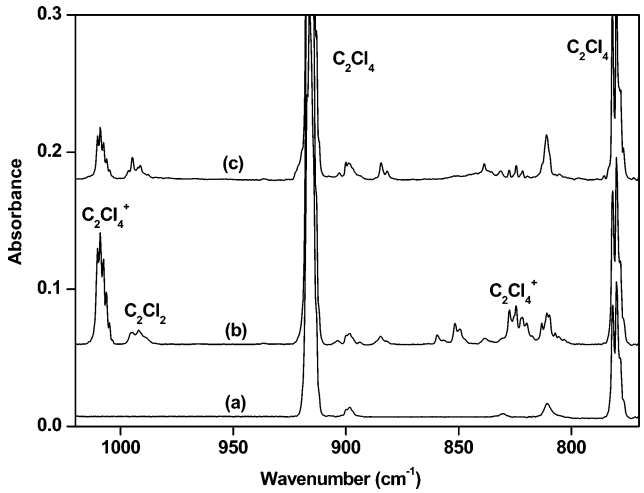

Figure 1. Infrared spectra in the 1020−770 cm^{-1} region from (a) 1 h of 0.02% C_2Cl_4/Ar sample deposition at 4 K, (b) 0.02% C_2Cl_4/Ar co-deposited with high-frequency-discharged Ar for 1 h, and (c) 20-min broad-band irradiation ($250 < \lambda < 580$ nm) of sample b.

Experimental and Computational Methods

The chlorinated ethylene cations were prepared by high-frequency discharge. The experimental setup for high-frequency discharge and matrix isolation infrared spectroscopic investigation has been described in detail previously.[24] Briefly, two gas streams containing pure argon and chlorinated ethylene/Ar mixtures were co-deposited with an approximately equal amount onto a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. The pure argon gas stream was subjected to discharge with a high-frequency generator (Telsa coil). The tip of telsa coil was connected to a copper cap on one end of a quartz tube extending into a vacuum chamber.

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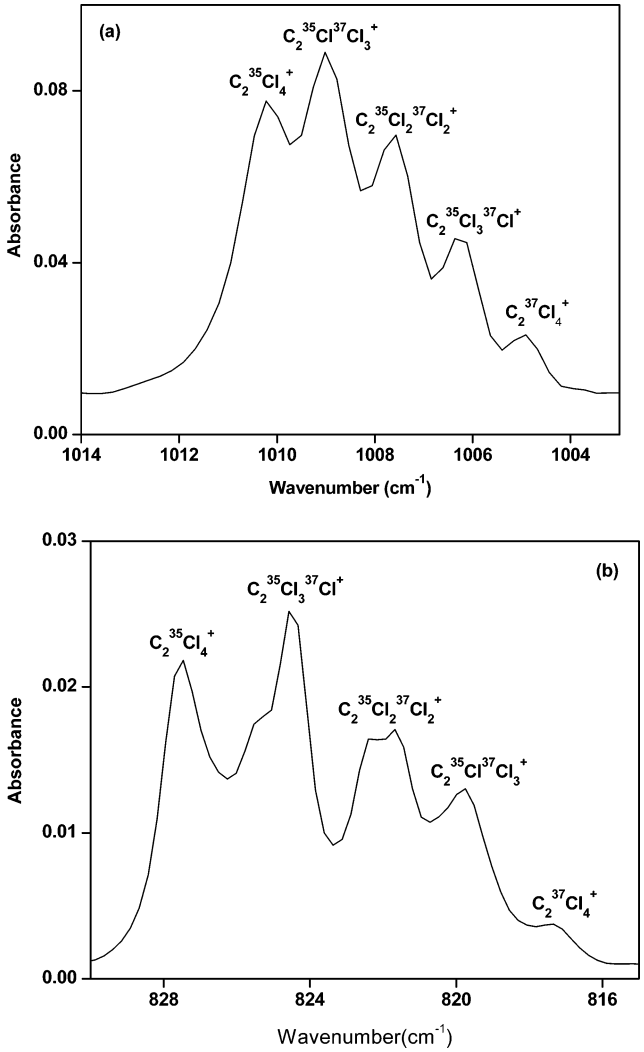

Figure 2. Infrared spectra in the (a) 1014−1005 and (b) 830−815 cm^{-1} regions from co-deposition of 0.02% C_2Cl_4/Ar with high-frequency-discharged Ar showing the isotopic splittings of the $C_2Cl_4{}^+$ cation absorptions.

The other end of the quartz tube was connected to a copper tube with ground potential. Discharge took place between the cap and the copper tube. The chlorinated ethylene/Ar mixtures were prepared in a stainless steel vacuum line using standard manometric technique. Tetrachloroethylene (Aldrich, 99%), trichloroethylene (Aldrich, 99.5%), 1,1-dichloroethylene (Aldrich, 99%), and *trans*-dichloroethylene (Aldrich, 98%) were used in different experiments. The chlorinated ethylenes were cooled to 77 K using liquid N_2 and were evacuated to remove volatile impurities. The infrared absorption spectra of the resulting samples were recorded on a Bruker Equinox 55 spectrometer at a resolution of 0.5 cm^{-1} between 4000 and 400 cm^{-1} using a DTGS detector. Matrix samples were annealed and subjected to broad-band irradiation using a high-pressure mercury arc lamp.

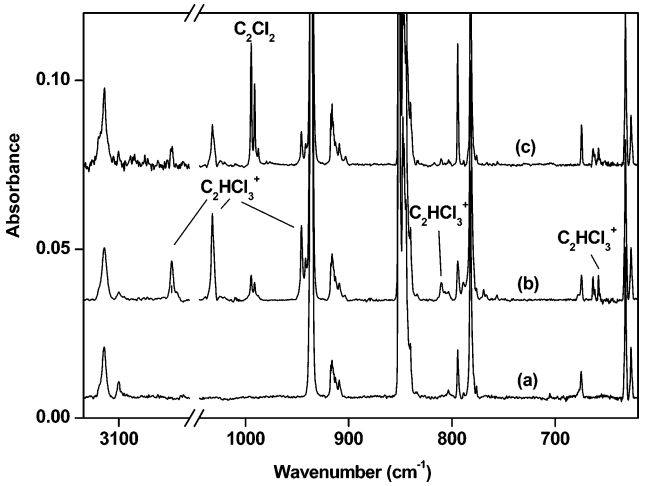

Figure 3. Infrared spectra in the 3125−3050 and 1045−620 cm^{-1} regions from (a) 1 h of 0.02% C_2HCl_3/Ar sample deposition at 4 K, (b) 0.02% C_2HCl_3/Ar co-deposited with high-frequency-discharged Ar for 1 h, and (c) 20-min broad-band irradiation ($250 < \lambda < 580$ nm) of sample b.

Quantum chemical calculations were performed using the Gaussion 03 program.[25] The Becke's three-parameter hybrid functional with the Lee−Yang−Parr correlation corrections (B3LYP) as well as the second-order Moller−Plesset perturbation theory (MP2) were used.[26,27] The 6-311++G(d, p) basis set was used for all calculations.[28] The geometries were fully optimized; the harmonic vibrational frequencies were calculated with analytic second derivatives. Anharmonic frequencies were also calculated for comparison.

Results and Discussion

In the present experiments, high-frequency discharge was employed to produce the chlorinated ethylene cations. Experiments were performed under a variety of experimental conditions. The product absorptions depend strongly on the power levels of discharge. Our recent experiments show that fragmentation dominates at high power of discharge, while the charged species become obvious when relatively low power was employed.[29] Therefore, we employ relatively low power of discharge to optimize the relative yield of the cation absorptions.

TABLE 1: Comparison of Calculated and Experimentally Observed Vibrational Frequencies (cm^{-1}) of the $C_2Cl_4{}^+$ Cation[a]

mode			B3LYP		MP2			
			harm	anharm	harm	anharm	Ar, 4 K	gas phase[b]
ν_1	a_g		1344.3 (0)	1315.9	1381.7 (0)	1358.6		1320 ± 80
ν_{10}	b_{3g}		1071.9 (0)	1052.5	1141.7 (0)	1141.9		
ν_8	b_{2u}	$C_2{}^{35}Cl_4$	986.7 (340)	965.7	1061.2 (500)	1042.8	1010.2	
		$C_2{}^{35}Cl_3{}^{37}Cl$	985.4		1059.9		1009.0	
		$C_2{}^{35}Cl_2{}^{37}Cl_2$	984.1		1058.5		1007.6	
		$C_2{}^{35}Cl^{37}Cl_3$	982.9		1057.1		1006.1	
		$C_2{}^{35}Cl_4$	981.6		1055.8		1004.9	
ν_5	b_{1u}	$C_2{}^{35}Cl_4$	816.7 (117)	799.3	881.0 (61)	879.1	827.5	
		$C_2{}^{35}Cl_3{}^{37}Cl$	815.2		879.2		824.6	
		$C_2{}^{35}Cl_2{}^{37}Cl_2$	813.6		877.5		821.6	
		$C_2{}^{35}Cl^{37}Cl_3$	812.0		875.6		819.7	
		$C_2{}^{35}Cl_4$	810.5		873.9		817.2	

[a] The calculated frequencies are unscaled and the intensities are listed in parentheses. [b] From ref 4.

TABLE 2: Comparison of Calculated and Experimentally Observed Vibrational Frequencies (cm^{-1}) of the $C_2HCl_3^+$ Cation[a]

mode		B3LYP		MP2			
		harm	anharm	harm	anharm	Ar, 4 K	gas phase[b]
ν_1	a′	3189.3 (40)	3067.4	3232.9 (37)	3107.7	3062.8	3073
ν_2	a′	1417.6 (3)	1384.4	1462.8 (1)	1435.6		1408
ν_3	a′	1297.2 (14)	1270.7	1336.5 (21)	1309.5		1267
ν_4	a′	1022.3 (129)	1002.3	1098.8 (195)	1077.0	1032.3	1038
ν_5	a′	935.0 (184)	917.6	1017.6 (236)	1003.7	945.9	990
ν_{10}	a″	810.3 (18)	817.8	797.9 (20)	848.5	810.6	875
ν_6	a′	656.1 (28)	647.1	686.1 (26)	677.8	658.3	660
ν_{11}	a″	476.5 (5)	477.6	452.4 (5)	492.7		472
ν_7	a′	405.3 (1)	400.3	421.5 (2)	418.2		402
ν_8	a′	296.4 (0.2)	289.7	307.9 (0.3)	307.5		286
ν_9	a′	184.7 (0.9)	183.1	192.6 (0.7)	190.5		180
ν_{12}	a″	143.7 (4)	149.9	132.5 (3)	147.3		148

[a] The calculated frequencies are unscaled and the intensities are listed in parentheses. [b] From ref 9 and 11.

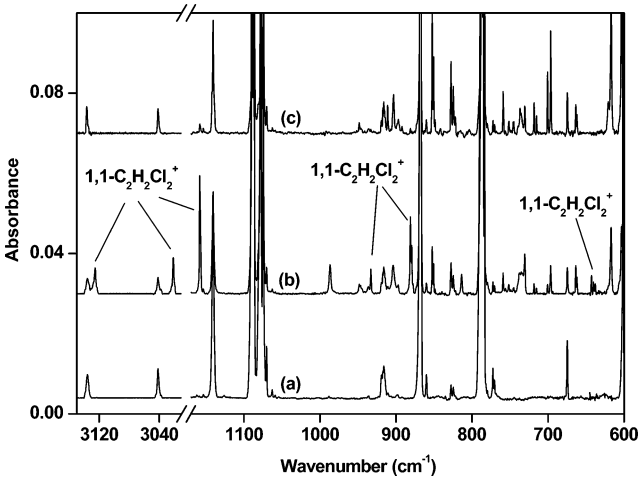

Figure 4. Infrared spectra in the 3150−3010 and 1170−600 cm^{-1} regions from (a) 1 h of 0.02% 1,1-$C_2H_2Cl_2$/Ar sample deposition at 4 K, (b) 0.02% 1,1-$C_2H_2Cl_2$/Ar co-deposited with high-frequency-discharged Ar for 1 h, and (c) 20-min broad-band irradiation ($250 < \lambda < 580$ nm) of sample b.

$C_2Cl_4^+$. The infrared spectra in the 1020−770 cm^{-1} frequency region from the experiment with 0.02% C_2Cl_4 in argon are shown in Figure 1. Trace a shows the spectrum taken after 1 h deposition of 0.02% C_2Cl_4 in argon at 4 K without discharge, while traces b and c show the spectra from another experiment of the 0.02% C_2Cl_4 in argon co-deposited with discharged Ar at 4 K. After 1 h of sample deposition at 4 K (trace b), new absorptions at 994.6, 991.1, and 987.6 cm^{-1} were observed. These absorptions were previously assigned to different isotopomers of C_2Cl_2.[30] In addition, new absorptions were observed as two quintets at 1010.2/1009.0/1007.6/1006.1/1004.9 cm^{-1} and 827.5/824.6/821.6/819.7/817.2 cm^{-1}, which were almost destroyed upon 20 min of broad-band irradiation (250 nm $< \lambda <$ 580 nm, trace c).

The two quintets at 1010.2/1009.0/1007.6/1006.1/1004.9 cm^{-1} and 827.5/824.6/821.6/819.7/817.2 cm^{-1} can be grouped together and are due to different vibrational modes of the same species. These absorptions are photosensitive and were produced only in the high-frequency discharge experiments, which suggest that the absorptions are due to a charged species. As shown in Figure 2, the five closely spaced absorptions are due to chlorine isotopic splittings which require the involvement of multiple chlorine atoms. The band positions of these two quintets are about 92.8 and 45.8 cm^{-1}, respectively, above the ClCCl antisymmetric (b_{2u}) and ClCCl symmetric (b_{1u}) stretching vibrational modes of the neutral C_2Cl_4 molecule in solid argon. The contour of the quintets is about the same as that of the antisymmetric and symmetric ClCCl stretching vibrations of the neutral C_2Cl_4 molecules. Accordingly, we assign the two quintets to the ClCCl antisymmetric and symmetric stretching modes of different isotopomers of $C_2Cl_4^+$ cation.

Theoretical calculations were performed on the $C_2Cl_4^+$ cation. For comparison, the neutral molecule was also calculated. The optimized structures are shown in Figure 6, and the vibrational frequencies and intensities are listed in Table 1. As can be seen in Figure 6, calculations at the B3LYP level gave slightly longer C−Cl bond length and shorter C−C bond length than those calculated at the MP2 level. The calculated C−C bond length of the cation is longer, whereas the C−Cl bond length is shorter than those of the neutral molecule calculated at the same level of theory. As listed in Table 1, the harmonic ClCCl stretching vibrational frequencies of the cation were calculated at 1061.2 and 881.0 cm^{-1} at the MP2 level and at 986.7 and 816.7 cm^{-1} with B3LYP. The anharmonic frequencies are slightly lower than the harmonic values. The vibrational frequencies are underestimated at the B3LYP level.[31] Considering the fact that the ratio for the natural abundance of ^{35}Cl to that of ^{37}Cl is 0.76/0.24, the ClCCl stretching vibration of $C_2Cl_4^+$ which involves four equivalent Cl atoms should split into five absorptions ($C_2{}^{35}Cl_4^+$, $C_2{}^{35}Cl_3{}^{37}Cl^+$, $C_2{}^{35}Cl_2{}^{37}Cl_2^+$, $C_2{}^{35}Cl^{37}Cl_3^+$, and $C_2{}^{37}Cl_4^+$) with approximately 81:108:54:12:1 relative intensities. As listed in Table 1, the calculated chlorine isotopic shifts are also in quite good agreement with the experimental values. An earlier photoelectron spectroscopic study in the gas phase yielded a C−C stretching frequency of the $C_2Cl_4^+$ cation at 1320 ± 80 cm^{-1}.[4] This mode is IR inactive and the anharmonic value was calculated to be 1358.6 cm^{-1} (MP2) and 1325.9 cm^{-1} (B3LYP).

$C_2HCl_3^+$. Figure 3 shows the spectra in the 3125−3050 and 1045−620 cm^{-1} regions from co-deposition of 0.02% C_2HCl_3/Ar with high-frequency-discharged argon. After 1 h of sample deposition, absorptions due to chloroacetylene (C_2HCl) at 3326.6 and 605.4 cm^{-1}, C_2Cl_2−HCl complex at 2789.4 and 2237.0 cm^{-1}, and dichloroacetylene at 994.6/991.1/987.6 cm^{-1} were observed.[30,32] These absorptions also can be produced by broad-band ($250 < \lambda < 580$ nm) irradiation of the 0.02% C_2HCl_3/Ar sample without discharge. In addition, new absorptions were observed at 3062.8, 1032.3, 945.9, 941.9, 810.6, and 658.3 cm^{-1}, which markedly decreased upon $250 < \lambda < 580$ nm irradiation. Weak absorptions at 615.8, 520.1, and 517.4 cm^{-1} (not shown) were observed after sample deposition and disappeared upon broad-band irradiation.

The 3062.8, 1032.3, 945.9, 941.9, 810.6, and 658.3 cm^{-1} absorptions are assigned to different vibrational modes of the $C_2HCl_3^+$ cation. The 3062.8 cm^{-1} band lies in the region

TABLE 3: Comparison of Calculated and Experimentally Observed Vibrational Frequencies (cm^{-1}) of the 1,1-$C_2H_2Cl_2^+$ Cation[a]

mode		B3LYP		MP2			
		harm	anharm	harm	anharm	Ar, 4 K	gas phase[b]
ν_9	b_2	3259.8 (24)	3115.0	3325.1 (24)	3189.7	3125.7	
ν_1	a_1	3140.6 (42)	3022.0	3192.9 (47)	3081.9	3021.1	
ν_2	a_1	1484.5 (27)	1450.7	1519.5 (24)	1471.7		
ν_3	a_1	1322.7 (3)	1296.0	1366.1 (9)	1340.6		1290 ± 80
ν_{10}	b_2	1156.2 (102)	1130.2	1219.2 (225)	1195.3	1158.1	
ν_7	b_1	948.1 (22)	972.2	895.9 (26)	1032.5	933.1	
ν_{11}	b_2	872.0 (107)	861.8	923.8 (151)	909.1	881.1	
ν_4	a_1	642.5 (24)	633.2	681.8 (22)	672.4	642.8	560 ± 80
ν_8	b_1	481.7 (5)	507.0	464.7 (4)	539.6		
ν_{12}	b_2	369.9 (5)	364.4	372.4 (7)	369.3		
ν_6	a_2	345.5 (0)	387.6	349.2 (2)	347.5		
ν_5	a_1	330.9 (2)	328.6	331.2 (0)	362.3		

[a] The calculated frequencies are unscaled and the intensities are listed in parentheses. [b] From ref 4−7.

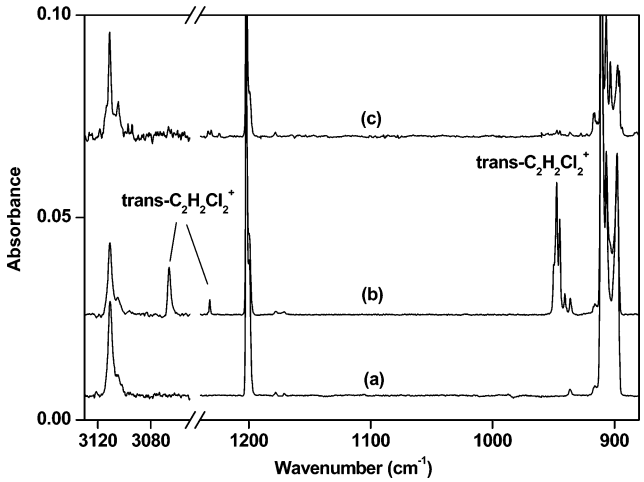

Figure 5. Infrared spectra in the 3130−3050 and 1240−880 cm^{-1} regions from (a) 1 h of 0.02% *trans*-$C_2H_2Cl_2$/Ar sample deposition at 4 K, (b) 0.02% $C_2H_2Cl_2$/Ar co-deposited with high-frequency-discharged Ar for 1 h, and (c) 20-min broad-band irradiation ($250 < \lambda < 580$ nm) of sample b.

expected for a H−C= stretching vibration, which is 47.7 cm^{-1} lower than the C−H stretching mode of the C_2HCl_3 neutral molecule. The 1032.3 cm^{-1} band is due to the antisymmetric ClCCl stretching vibration. The band is broad because of unresolved chlorine isotopic splittings. The relative intensities of the 945.9 and 941.9 cm^{-1} absorptions match natural isotopic abundance chlorine. These two absorptions are due to the C−Cl stretching vibrations of the $CH^{35}ClCCl_2^+$ and $CH^{37}ClCCl_2^+$ cations. The 810.6 cm^{-1} is due to the out-of-plane C−H bending vibration. The 658.3 cm^{-1} absorption is the symmetric ClCCl stretching mode, and the chlorine isotopic splittings cannot be resolved.

Recently, the $C_2H^{35}Cl_3^+$ cation has been spectroscopically studied in the gas phase.[9,11] All 12 fundamental vibrational frequencies were determined to be 3073, 1408, 1267, 1038, 990, 875, 660, 472, 402, 286, 180, and 148 cm^{-1}, respectively. Only five modes were observed in the present experiment in solid argon. The other modes are either too low in intensity or out of the spectral range of our spectrometer. The observed frequencies of the $C_2H^{35}Cl_3^+$ cation in solid argon are red-shifted by 0.3%, 0.5%, 4.5%, 7.4%, and 0.3%, respectively, from the gas-phase values. The $C_2HCl_3^+$ cation has a $^2A''$ ground state. The optimized geometric parameters are shown in Figure 6, and the vibrational frequencies are listed in Table 2. Similar to the $C_2Cl_4^+$ cation, the B3LYP calculations slightly underestimated the C−Cl stretching vibrational frequencies. There is quite a large deviation between the gas phase and the matrix values for the C−Cl stretching and out-of-plane C−H bending modes. The gas-phase values reported at 990 and 875 cm^{-1} are substantially higher than the matrix values of 945.9 and 810.6 cm^{-1}. The shifts for the other modes are less than 0.5%. The calculated frequencies (Table 2) also suggest that the gas-phase values for these two modes may be incorrect. Take the out-of-plane C−H bending mode for example. The harmonic frequency of this mode was predicted at 810.3 cm^{-1} (B3LYP) and 797.9 cm^{-1} (MP2), very close to the argon matrix value of 810.6 cm^{-1}. As a reference point, the harmonic C−H bending mode of the C_2HCl_3 neutral was predicted to be 804.9 cm^{-1} (B3LYP) and 763.2 cm^{-1} (MP2), which was observed at 782.1 cm^{-1} in solid argon. The anharmonic values are higher than the harmonic values but still are quite lower than the gas-phase value.

1,1-$C_2H_2Cl_2^+$. Similar experiments were also performed using a 0.02% 1,1-$C_2H_2Cl_2$ in argon. The infrared spectra in the 3150−3010 and 1170−600 cm^{-1} regions are illustrated in Figure 4. After 1 h of sample deposition with discharge, absorptions due to the C_2HCl−HCl complex at 3314.3, 2782.2, 2102.2, 759.1, 617.1, and 603.5 cm^{-1};[30,33] *trans*-dichloroethylene at 1200.8, 911.1, and 827.7/824.6/821.9 cm^{-1};[32] *cis*-dichloroethylene at 1593.8, 1300.8, 852.3/850.6/848.7, 718.3/715.2/712.0, and 700.6/696.6 cm^{-1};[32] and HAr_2^+ at 903.1 cm^{-1} [34] were observed. In addition, a group of new absorptions at 3125.7, 3021.1, 1158.1, 933.1, 881.1, 879.3, 877.6, 642.8, 640.2, and 637.8 cm^{-1} were also observed. These new absorptions disappeared upon 20 min of broad-band ($250 < \lambda < 580$ nm) irradiation. Another experiment was done using 0.05% 1,1-dichloroethylene in argon without discharge. After deposition, the sample was subjected to 45 min of $250 < \lambda < 580$ nm irradiation. The C_2HCl−HCl complex, *trans*-dichloroethylene, and *cis*-dichloroethylene absorptions were produced. However, the HAr_2^+ absorption and the group of new absorptions at 3125.7, 3021.1, 1158.1, 933.1, 881.1, 879.3, 877.6, 642.8, 640.2, and 637.8 cm^{-1} were not observed.

The photosensitive absorptions at 3125.7, 3021.1, 1158.1, 933.1, 881.1, 879.3, 877.6, 642.8, 640.2, and 637.8 cm^{-1}, which were only produced in the discharge experiments, are assigned to the 1,1-$C_2H_2Cl_2^+$ cation. The 3125.7 and 3021.1 cm^{-1} absorptions are due to C−H stretching vibrations. The observation of two C−H stretching vibrations indicates the involvement of two C−H subunits. The 881.1, 879.3, and 877.6 cm^{-1} absorptions exhibit approximately 9:6:1 relative intensities, indicating the involvement of two equivalent chlorine atoms. These three absorptions are due to antisymmetric ClCCl stretching vibrations of different $C_2H_2Cl_2$ isotopomers. The 642.8, 640.2, and 637.8 cm^{-1} absorptions also show ap-

TABLE 4: Comparison of Calculated and Experimentally Observed Vibrational Frequencies (cm^{-1}) of the *trans*-$C_2H_2Cl_2^+$ Cation[a]

mod e		B3LYP		MP2			
		harm	anharm	harm	anharm	Ar, 4 K	gas phase[b]
ν_1	a_g	3184.6 (0)	3047.7	3225.3 (0)	3103.4		
ν_9	b_u	3184.2 (56)	3045.2	3224.2 (51)	3099.0	3066.1	3068
ν_2	a_g	1468.8 (0)	1430.0	1513.5 (0)	1477.1		1452
ν_3	a_g	1283.2 (0)	1256.4	1309.2 (0)	1271.4		1258
ν_{10}	b_u	1272.2 (7)	1247.5	1312.4 (10)	1285.5	1231.9	1235
ν_{11}	b_u	944.6 (185)	927.7	1043.2 (279)	1028.6	950.1	955
ν_4	a_g	940.8 (0)	925.1	1010.4 (0)	994.9		943
ν_8	b_g	864.5 (0)	859.4	862.1 (0)	881.3		873
ν_6	a_u	857.4 (53)	833.3	882.5 (57)	862.4	840.0	836
ν_5	a_g	364.6 (0)	364.1	377.9 (0)	377.3		368
ν_{12}	b_u	250.6 (8)	251.6	257.8 (7)	258.3		251
ν_7	a_u	162.8 (5)	161.5	159.6 (4)	164.5		163

[a] The calculated frequencies are unscaled and the intensities are listed in parentheses. [b] From ref 10 and 13.

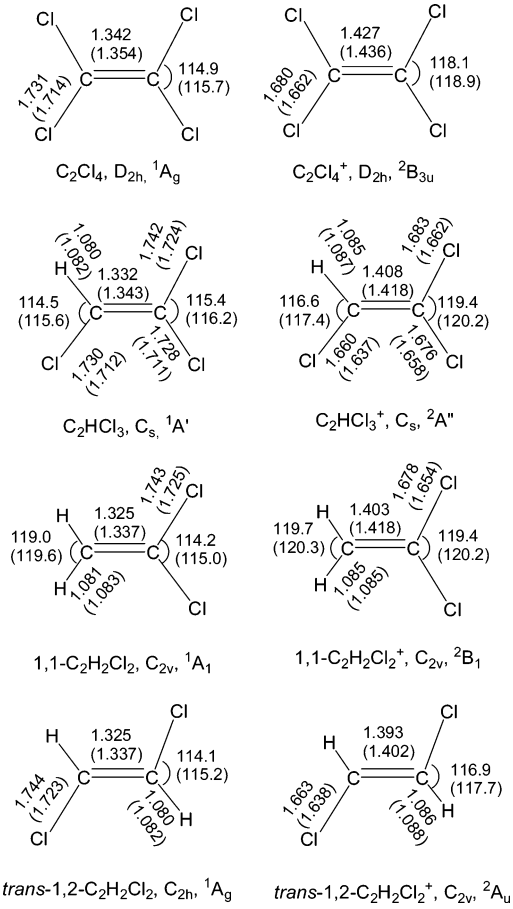

Figure 6. Optimized structures (bond lengths in Å, bond angles in degrees) of the chlorinated ethylene neutrals and cations at the B3LYP/6-311++G(d, p) and MP2/6-311++G(d, p) (in parentheses) levels of theory.

proximately 9:6:1 relative intensities and are due to the symmetric ClCCl stretching vibrations of different $C_2H_2Cl_2$ isotopomers. The 1158.1 and 933.1 cm^{-1} absorptions do not exhibit obvious chlorine isotopic splitting and are due to the CH_2 in-plane wagging and out-of-plane bending vibrations.

The harmonic and anharmonic vibrational frequencies of the ground-state 1,1-$C_2H_2Cl_2^+$ cation calculated at both levels of theory are listed in Table 3, which are in reasonable agreement with the experimental values. In addition, the calculations also predicted that the chlorine isotopic shifts agree well with the experimental values. For example, the chlorine isotopic shifts for the antisymmetric and symmetric ClCCl stretching modes were predicted to be -1.8 and -3.7 cm^{-1} (antisymmetric) and -4.3 and -8.6 cm^{-1} (symmetric) with B3LYP. The experimentally observed shifts are -1.8 and -3.5 cm^{-1} (antisymmetric) and -2.6 and -5.0 cm^{-1} (symmetric). The 1,1-$C_2H_2Cl_2^+$ cation was previously studied in the gas phase using the photoelectron spectroscopy.[4−7] The C═C stretching and symmetric ClCCl stretching modes were determined to be 1290 and 560 cm^{-1} with 80 cm^{-1} uncertainty. The C═C stretching mode was not observed in the present study because of IR weakness. The anharmonic value of this mode was predicted to be 1340.6 cm^{-1} (MP2) and 1296.0 cm^{-1} (B3LYP).

***trans*-$C_2H_2Cl_2^+$.** Figure 5 shows the spectra in the 3130−3050 and 1240−880 cm^{-1} regions using a 0.02% *trans*-$C_2H_2Cl_2$ in argon sample. Besides the known absorptions due to the C_2HCl−HCl complex,[30,32,33] *cis*-1,2-dichloroethylene and acetylene, new absorptions at 3066.1, 1231.9, 950.1, 947.3, 944.9, 862.9, 861.2, 859.5, and 840.0 cm^{-1}, were observed after 1 h of sample deposition with discharge. The 3066.1, 1231.9, 950.1, 947.3, 944.9, and 840.0 cm^{-1} absorptions were destroyed, while the 862.9, 861.2, and 859.5 cm^{-1} absorptions markedly increased upon broad-band ($250 < \lambda < 580$ nm) irradiation. Another experiment was done using 0.05% 1,1-dichloroethylene in argon without discharge. After deposition, the sample was subjected to 45 min of $250 < \lambda < 580$ nm irradiation. The C_2HCl−HCl complex, *cis*-dichloroethylene, and C_2H_2 absorptions as well as the 862.9, 861.2, and 859.5 cm^{-1} absorptions were produced. However, the absorptions at 3066.1, 1231.9, 950.1, 947.3, 944.9, and 840.0 cm^{-1} were not produced.

The photosensitive absorptions at 3066.1, 1231.9, 950.1, 947.3, 944.9, and 840.0 cm^{-1} are assigned to the *trans*-$C_2H_2Cl_2^+$ cation. The 3066.1 cm^{-1} absorption is due to the antisymmetric C−H stretching mode. The symmetric C−H stretching mode is IR inactive. The 1231.9 cm^{-1} absorption is sharp and does not show chlorine isotopic splitting. This band is due to the out-of-plane CH bending vibration. The 950.1, 947.3, and 944.9 cm^{-1} absorptions are due to antisymmetric C−Cl stretching mode of the $C_2H_2{}^{35}Cl_2^+$, $C_2H_2{}^{35}Cl^{37}Cl^+$, and $C_2H_2{}^{37}Cl_2^+$ isotopomers. These three absorptions exhibit approximately 9:6:1 relative intensities. The 840.0 cm^{-1} absorption also exhibits no obvious chlorine isotopic splitting and is assigned to the out-of-plane CH bending vibration of the cation. As listed in Table 4, the above-characterized vibrational modes are IR active with appreciable intensities. All the other modes are either IR inactive or have very low IR intensities and were not observed in the experiments.

Recently, the *trans*-$C_2H_2{}^{35}Cl_2^+$ cation was studied in the gas phase. Eleven vibrational fundamentals of the cation were reported.[10,13] The four vibrational modes observed in solid argon were reported at 3068, 1235, 955, and 836 cm^{-1} in the gas

TABLE 5: Comparison of the Vibrational Absorptions (cm^{-1}) of Chlorinated Ethylene Cations and Neutrals in Solid Argon

		mode	cation	neutral
C_2Cl_4	ν_8	asym C−Cl str.	1010.2	917.4
	ν_5	sym C−Cl str.	827.5	781.7
	ν_1	C−H str.	3062.8	3110.5
	ν_4	asym. C−Cl str.	1032.3	936.7
C_2HCl_3	ν_5	C−Cl str.	945.9	851.8
	ν_{10}	CH out-of-plane bend.	810.6	782.1
	ν_6	sym. C−Cl str.	658.3	632.2
	ν_9	asym. C−H str.	3125.7	3135.8
	ν_1	sym. C−H str.	3021.1	3041.5
1,1-$C_2H_2Cl_2$	ν_{10}	CH in-plane wag.	1158.1	1089.3
	ν_7	CH out-of-plane bend.	933.1	868.0
	ν_{11}	asym. C−Cl str.	881.1	787.4
	ν_4	sym. C−Cl str.	642.8	601.3
	ν_9	asym. C−H str.	3066.1	3110.8
trans-$C_2H_2Cl_2$	ν_{10}	CH in-plane bend.	1231.9	1201.9
	ν_{11}	asym. C−Cl str.	950.1	827.7
	ν_6	CH out-of-plane bend.	840.0	911.1

phase. The argon matrix values are only about −1.9, −3.1, −4.9, and +4.0 cm^{-1} shifted from the gas-phase positions.

All the four chlorinated ethylene neutral molecules have a singlet ground state, while the cations have an open-shell doublet ground state. As shown in Figure 6, the calculated C═C and C−H bond lengths of the cations are longer than those of the corresponding neutrals, whereas the C−Cl bond lengths are shorter than those of the neutrals. The HOMO of the chlorinated ethylene neutrals is a π orbital with C═C bonding and C−Cl antibonding in character. Therefore, the removal of one electron from this orbital elongates the C═C bond length and shortens the C−Cl bond lengths, which result in a red-shift of the C═C stretching vibrational frequencies and a blue-shift of the C−Cl stretching vibrational frequencies. As can be seen in Table 5, the C−Cl stretching vibrational frequencies of the cations are higher than those of the neutrals.

Recent investigations have shown that some cations trapped in solid argon matrix are coordinated by multiple argon atoms in forming the cation−noble gas complexes.[35,36] To determine whether the cations trapped in solid argon are coordinated by noble gas atoms or not, experiments were performed by using mixtures of argon doped with xenon. If a cation is coordinated by argon atoms, xenon can replace the coordinated argon atoms, which will induce shifts of the vibrational frequencies of the cation. No new absorptions were observed in the experiments with xenon doped into argon, suggesting that the above-characterized chlorinated ethylene cations are not coordinated by argon and can be regarded as the "isolated" species. The gas-phase vibrational frequencies of the $C_2HCl_3^+$ and *trans*-$C_2H_2Cl_2^+$ cations are reported,[9−13] which can be compared to the argon matrix values. The matrix shifts for the vibrational modes of *trans*-$C_2H_2Cl_2^+$ are less than 0.6%. The observed frequencies of the $C_2H^{35}Cl_3^+$ cation in solid argon are red-shifted by 0.3%, 0.5%, 4.5%, 7.4%, and 0.3%, respectively, from the gas-phase values. As has been discussed above, the gas-phase values for the C−Cl stretching and out-of-plane C−H bending modes are probably overestimated.

Conclusions

The chlorinated ethylene cations $C_2Cl_4^+$, $C_2HCl_3^+$, 1,1-$C_2H_2Cl_2^+$, and *trans*-$C_2H_2Cl_2^+$ have been produced by co-deposition of the chlorinated ethylene neutrals with high-frequency-discharged Ar at 4 K. The infrared spectra of the resulting products in solid argon are recorded. Photosensitive absorptions are assigned to different vibrational modes of the chlorinated ethylene cations on the basis of chlorine isotopic shifts and theoretical frequency calculations. With the removal of one electron from the HOMO of chlorinated ethylene neutrals that is C═C bonding and C−Cl antibonding in character, the C═C bond is weakened, while the C−Cl bond is strengthened, and hence, the C−Cl vibrational frequencies of the cations are blue-shifted relative to those of the neutrals. The vibrational frequencies of the $C_2HCl_3^+$ and *trans*-$C_2H_2Cl_2^+$ cations in the gas phase were recently reported. The observed frequencies in solid argon are only very slightly shifted from the gas-phase values except the C−Cl stretching and out-of-plane C−H bending modes of the $C_2HCl_3^+$ cation. We suggest that the gas-phase values of these two modes are in error. The experiments with xenon doped into argon also suggest that the cations in solid argon are not coordinated by argon atoms and can be regarded as the isolated cations in solid argon.

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