

Long-Lived Excited Electronic States of the Dichloroethylene Cation Isomers Probed by Charge Exchange Ionization

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Charge exchange technique has been used to detect the presence of long-lived excited electronic states of trans-, cis-, and 1,1-C₂H₂Cl₂⁺. The \tilde{B} states of the three cations which are formed by removal of an electron from an in-plane chlorine nonbonding orbital of the corresponding neutrals have been found to have long lifetimes (tens of microseconds or longer). Whether the \tilde{A} states formed by removal of an electron from the other in-plane chlorine nonbonding orbitals are long-lived also can not be determined by the present experiments. Cations in the excited electronic states above the \tilde{B} states were not detected because of their prompt dissociation following intramolecular relaxation or radiative decay. (J Am Soc Mass Spectrom 2004, 15, 1266–1273) © 2004 American Society for Mass Spectrometry

Investigation of the properties of excited electronic states is one of the frontier research subjects in chemistry, physics, and related fields [1–4]. For example, accurate calculation of excited state properties is one of the major research efforts in the field of quantum chemistry. Reactions occurring in excited electronic states have also been investigated. Dynamics of polyatomic cations in excited electronic states have special relevance to the field of mass spectrometry because the theory of mass spectra hypothesizes very rapid internal conversion from excited electronic states to the ground electronic state in such systems [5]; that is to say, dissociation of a polyatomic cation is assumed to occur in the ground electronic state. Even though many exceptions to the above hypothesis were observed [6–15], most were due to rapid dissociation in repulsive excited states, prior to internal conversion [6–9]. Examples of very slow internal conversion [10, 11], or cases of very long-lived excited electronic states [12–21], were rare especially for polyatomic cations consisting of more than three atoms.

The first encounter with a very long-lived excited electronic state in this laboratory occurred in the photodissociation study of the benzene cation [22], which showed that its \tilde{A}^2E_{2g} state (often called \tilde{B}^2E_{2g} state) was

present 30 μ s after formation. Then, a more direct method based on the detection of charge exchange signal, B⁺, from a reagent (B) in a separate collision cell was developed to find the presence of a polyatomic cation (A⁺) in an excited electronic state [23].



$$\Delta E = IE(B) - RE(A^+) \quad (2)$$

Here IE is the ionization energy of B and RE is the recombination energy of A⁺. When the laboratory translational energy of A⁺ was kept at 100 eV or lower and the pressure of B inside the collision cell was adjusted such that the intensity of A⁺ was attenuated by ~20%, B⁺ with the intensity as large as a few percent of A⁺ was observed when the reaction was exoergic or resonant. The B⁺ intensity was significant until the reaction was endoergic by 0.1 eV [24], beyond which it decreased rapidly, by orders of magnitude. This exoergicity rule was utilized to determine RE of A⁺ and hence the highest electronic state surviving several microseconds after the ion formation; that is to say, charge exchange gases with different IEs were used and RE of A⁺ was estimated from the presence/absence of the prominent B⁺ signal.

In our initial search for the long-lived excited electronic states of polyatomic cations, those displaying well-resolved vibrational structures in the photoelectron spectra were the prime candidates. Accordingly, the \tilde{B}^2B_2 states of chlorobenzene, bromobenzene, ben-

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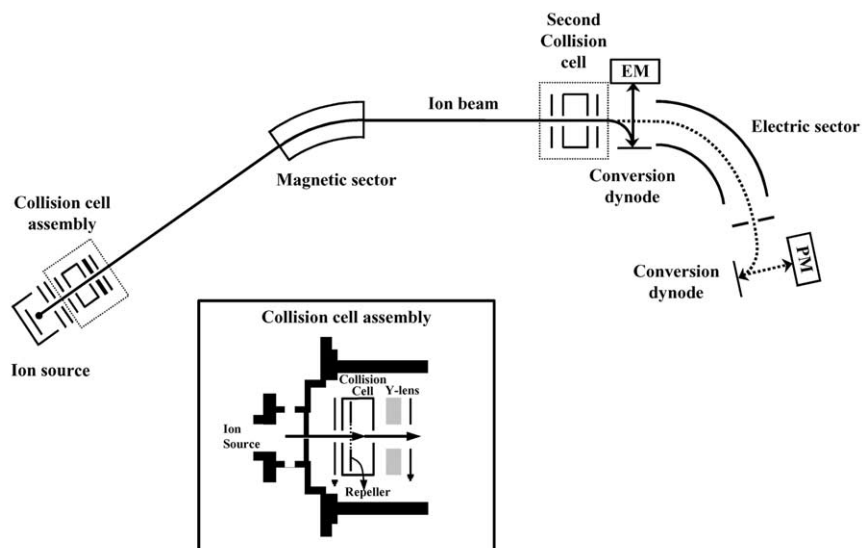


Figure 1. Diagram of the double focusing mass spectrometer with reversed geometry (VG Analytical ZAB-E). The inset shows details of the first charge exchange cell.

zonitrile, and phenylacetylene cations were found to be long-lived [25]. Similarly, the \tilde{A}^2A' states of vinylchloride, vinylbromide, vinyliodide, acrylonitrile cations were found to be long-lived [26]. A feature common to all these states is that they are generated by removal of an electron from an in-plane orbital, in-plane nonbonding p orbitals of halogens or in-plane π orbitals of triple bonds. In contrast, the ground states of these cations are generated by removal of an electron from the π systems which are perpendicular to the molecular plane.

Planar molecules with multiple halogen substitution have more than one in-plane nonbonding orbital and it would be interesting to see if the above correlation would also hold for such systems. Three isomers of dichloroethylene cations, trans, cis, and 1,1, have been investigated and are reported in this paper.

Experimental

1,1-, cis-1,2-, and trans-1,2-dichloroethylenes were purchased from TCI (Tokyo, Japan). Fluoromethane was purchased from Lancaster (Lancashire, UK) and other chemicals from Sigma (Milwaukee, WI). All the chemicals were of the highest purity commercially available and were used without further purification.

A diagram of the double focusing mass spectrometer with reversed geometry VG ZAB-E (Manchester, UK) is shown in Figure 1. The first collision cell located between the ion source and the magnetic sector was modified to optimize the detection of ions generated from the reagent gas inside the cell by charge exchange. Details of the modifications made were reported previously [23]. Sample was introduced to the ion source at 140 °C via a glass capillary connected to a reservoir ("septum inlet") and ionized under the electron ionization (EI) condition at 17 eV electron energy. Ions were

accelerated with high voltage (V_S) of 4 kV. Experimental conditions for the charge exchange in the first and second cells are the same. In each case, the cell was floated at high voltage, V_C and V_C' , respectively, such that the incoming ion had the translational energy of 50 ~100 eV inside the cell. Reagent gas pressure was adjusted to attenuate the incoming ion beam by ~20%, which was the upper limit of the single collision condition [27].

Methods of Reagent Ion Detection

Methods to identify ions generated from a reagent gas using a double focusing mass spectrometer with reverse geometry were developed previously [23, 25]. A brief account is as follows. Three types (I, II, and III) of ions exit the first collision cell, which can be differentiated by their translational energies, K_I , K_{II} , and K_{III} [28].

$$\text{Type I, } K_I = eV_S \quad (3)$$

$$\text{Type II, } K_{II} = e[V_C + (m_2/m_1)(V_S - V_C)] \quad (4)$$

$$\text{Type II, } K_{III} = eV_C \quad (5)$$

These are ions generated in the ion source (Type I), their collision-induced dissociation products generated inside the cell (Type II), and ions generated from the reagent gas inside the cell (Type III). The effective m/z of each ion in single focusing mass spectrometry can be calculated with

$$m/z = B^2 r^2 e^2 / 2K \quad (6)$$

Here, r is the magnet radius, B is the magnetic field, and

K is the translational energy, one of $K_I \sim K_{III}$. Since the electric sector is an energy analyzer, only ions of a particular type can be detected by setting the electric sector potential to transmit ions with the corresponding translational energy. To detect only the Type III ions, we set the electric sector potential to transmit ions with the translational energy eV_C even though the acceleration potential V_S is applied in the ion source. Then, the spectrum is recorded with the usual double focusing mode, namely by scanning the magnetic field and detecting ions with a detector located after the electric sector. This will be called eV_C double focusing mass spectrometry. Since the translational energies of Types I and II ions are different from eV_C , only Type III ions will be detected in the eV_C double focusing mode. The second scheme is to detect reagent gas ions generated inside the second cell using mass-analyzed ion kinetic energy spectrometry (MIKES) [29]; that is to say, the magnetic sector field is set to transmit the molecular ions generated inside the ion source and the electric sector potential is scanned. The ions generated from the reagent gas inside the second cell appear in the MIKE spectrum at the translational energy eV_C' . Identification of charge exchange processes is not as definitive as in the first cell experiments because m/z of the ions generated can not be determined in this scheme. The main utility of this scheme is to confirm that the molecular ion, not the fragment ions, generated in the source by EI is responsible for the charge exchange ionization occurring in the collision cells. Spectra were recorded using the two schemes in all the charge exchange investigations because the information obtained is complementary.

Results and Discussion

There are a few technical difficulties that can interfere with the present measurements. The first is the leakage of the reagent gas from the first cell to the ion source. The reagent gas ion, B^+ , generated in the ion source by EI is Type I and can be distinguished from the same ion generated in the cell (Type III). However, excessive generation of the Type I B^+ would lead to substantial Type III B^+ through symmetric charge exchange, $B^+ + B \rightarrow B + B^+$. As described in previous papers [23, 25], the first cell was designed to reduce the reagent gas leakage as much as possible. As shown in the inset of Figure 1, an additional slit was installed between the ion source chamber and the collision cell assembly evacuated by analyzer pumping system for this purpose. In the actual measurements, care was taken such that the Type I B^+ intensity was comparable to or less than the Type III intensity. The same slit restricted the gas leakage from the source to the first collision cell, so that we could hardly detect the Type III A^+ ions. The second difficulty arises from the fact that not only the molecular ion but some fragment ions are also generated by EI and enter the first cell. Odd electron fragment ions are especially troublesome because their recombi-

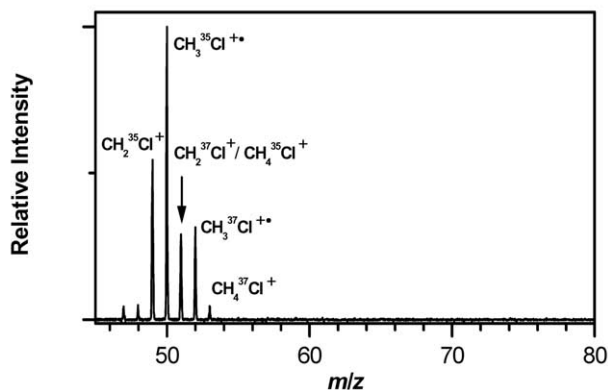


Figure 2. eV_C double focusing spectrum of $\text{trans-C}_2\text{H}_2\text{Cl}_2^+$ generated by 17 eV EI with CH_3Cl in the first cell. V_S and V_C were 4005 and 3939 V, respectively. All the peaks are due to Type III ions.

nation energies can be larger than that of the excited electronic state of the molecular ion being probed. In the 70 eV EI spectra of dichloroethylene isomers, C_2H_2^+ and C_2HCl^+ appear prominently and have recombination energies comparable to those of the first excited electronic states of the molecular ions. Lowering the electron energy to ~ 17 eV eliminated these ions almost entirely and was used throughout the study. $\text{C}_2\text{H}_2\text{Cl}^+$ was the only fragment ion appearing prominently in the 17 eV EI spectra with an intensity of $\sim 5\%$ relative to those of the molecular ions. Even though the presence of $\text{C}_2\text{H}_2\text{Cl}^+$ at this level was not expected to critically affect the present study, further checks were made. The recombination energy of $\text{C}_2\text{H}_2\text{Cl}^+$ is not available in the literature. Gaussian 98 G2 calculations [30] estimated the recombination energy as 8.80 eV, well below those of the three isomers of dichloroethylene cations in the ground electronic states. We also performed the second cell experiment for $\text{C}_2\text{H}_2\text{Cl}^+$ selected by the magnetic sector and confirmed that this ion would not affect our charge exchange experiments for the molecular ions.

Charge Exchange Experiments

Figure 2 shows the 17 eV EI mass spectrum of $\text{trans-1,2-dichloroethylene}$ ($\text{trans-C}_2\text{H}_2\text{Cl}_2$) recorded under eV_C double focusing conditions with CH_3Cl in the first cell. V_S and V_C were 4005 and 3939 V, respectively. Hence the translational energy of $\text{trans-C}_2\text{H}_2\text{Cl}_2^+$ inside the cell was 66 eV. Type III CH_3Cl^+ ions formed the main peaks in the spectrum. Type III CH_2Cl^+ and CH_4Cl^+ also appeared weakly in the spectrum, which might be the products of ion-molecule reactions [31] involving CH_3Cl^+ occurring inside the cell. Since the ionization energy of CH_3Cl is 11.28 ± 0.01 eV [32], much larger than the recombination energy of ~ 9.8 eV for $\text{trans-C}_2\text{H}_2\text{Cl}_2^+$ in the ground electronic state, it can be concluded through the exoergicity rule that some $\text{trans-C}_2\text{H}_2\text{Cl}_2^+$ ions entering the collision cell are in a long-lived excited state(s) which is at ~ 1.5 eV or higher above the ground state.

Table 1. Charge exchange gases used, their ionization energies (IE) in eV, and success/failure^a to observe charge exchange signals for some precursor ion/charge exchange gas combinations

Charge exchange gas	IE (eV)	Ref.	Precursor ions (C ₂ H ₂ Cl ₂ ⁺)		
			Trans	Cis	1.1
1,3-C ₄ H ₆	9.07 ± 0.02	28	O	O	O
CS ₂	10.07 ± 0.02	37	O	O	O
1,1-CH ₂ CF ₂	10.29 ± 0.01	38	O	O	O
CH ₃ Br	10.5 ± 0.01	39	O	O	O
CH ₃ Cl	11.28 ± 0.01	26	O	O	O
CH ₃ CClF ₂	11.98 ± 0.01	26	O	O	O
Xe	12.12 ± 0.02	29	X	X	O
CH ₃ F	12.50	30	X	X	X
CHF ₃	13.86	27	X	X	X

^aSuccess and failure indicated by O and X, respectively.

Similar spectra were recorded with reagent gases with widely different ionization energies as listed in Table 1. Intensities of the reagent gas ions relative to that of the incoming trans-C₂H₂Cl₂⁺ are plotted as a function of the reagent gas ionization energy in Figure 3a. The reagent ion intensity is substantial for reagent gases such as 1,3-butadiene which have an ionization energy [33] less than the recombination energy of trans-C₂H₂Cl₂⁺ in the ground state. As the former gets larger than the latter, the reagent ion signal decreases and disappears eventually. The charge exchange signal from Xe (IE = 12.12 ± 0.02 eV) [34] was a few percent of those from CH₃Cl (IE = 11.28 ± 0.01 eV) or CH₃CClF₂ (IE = 11.98 ± 0.01 eV) [32]. Invoking the exoergic rule, the data suggest the presence of a long-lived excited state of trans-C₂H₂Cl₂⁺ with the recombination energy a little below 12.12 eV. We also recorded the MIKE spectra by introducing the mass-selected C₂H₂Cl₂⁺ ion beam into the second cell filled with a reagent gas. Figure 4 shows such spectra recorded at two different values of the cell potential for trans-C₂H₂Cl₂⁺ entering the cell filled with CH₃Cl. The peaks marked by arrows in the spectra appear at the kinetic energy corresponding to the cell potential and must be due to ions from the reagent gas. The presence of these peaks confirms that trans-C₂H₂Cl₂⁺ is responsible for the charge exchange ionization of CH₃Cl. It takes ~30 μs for the molecular ion to fly from the ion source to the second cell. This may be taken as the virtual lower limit to the lifetime of the long-lived state involved. The remaining two peaks in each spectrum are due to collision-induced dissociation of the molecular ion to C₂H₂Cl⁺ and C₂H₂⁺.

The eV_C double focusing spectra recorded for cis-C₂H₂Cl₂⁺ using CH₃Br and CH₃CClF₂ as reagent gases are shown in Figure 5. The cis-C₂H₂Cl₂⁺/CH₃Br charge exchange result is similar to that of trans-C₂H₂Cl₂⁺/CH₃Cl. For CH₃CClF₂ reagent gas, its molecular ion was rather unstable and appeared very weakly. Instead, its stable fragments, CH₃CF₂⁺ and CH₂CF₂⁺, appeared prominently in the spectrum. Charge exchange signals from Xe and other reagent gases with higher ionization energy were either very weak or hardly observed, as

summarized in Table 1. The situation was somewhat different for 1,1-C₂H₂Cl₂⁺ (1,1-dichloroethylene cation), which ionized Xe (IE = 12.12 ± 0.02 eV) as shown in Figure 6 unlike the above two isomers. The charge

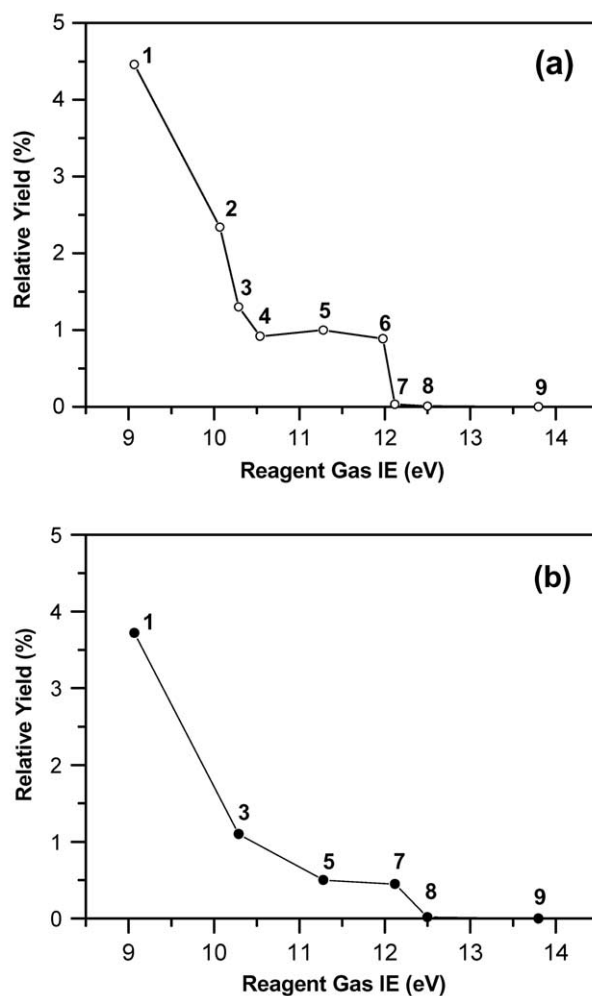


Figure 3. Intensities of the reagent gas ions relative to that of the incoming (a) trans-C₂H₂Cl₂⁺ and (b) 1,1-C₂H₂Cl₂⁺ plotted as a function of the reagent gas ionization energy. The reagent gases in Table 1 are numbered in order of increasing ionization energy.

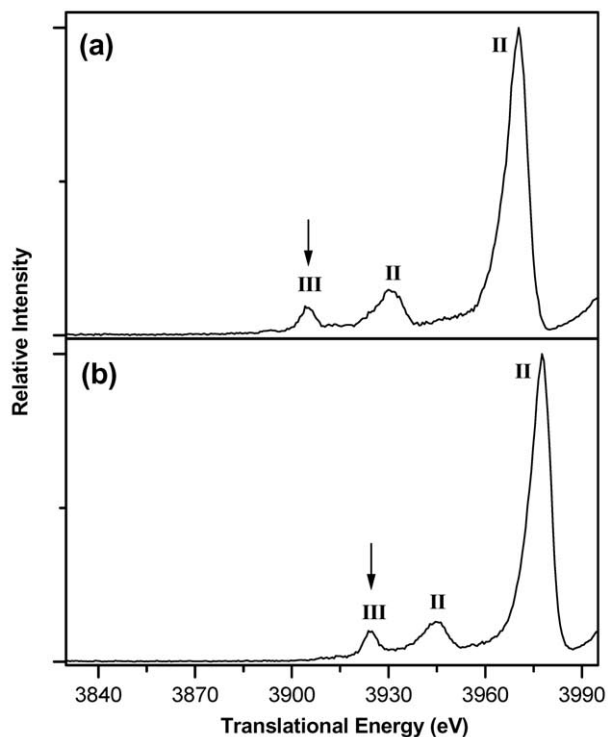


Figure 4. The MIKE spectra recorded with $\text{trans-C}_2\text{H}_2\text{Cl}_2^+$ entering the second cell filled with CH_3Cl . V_S was 4006 V. V_C was (a) 3906 and (b) 3925 V. The peaks marked by arrows arise from the reagent gas (CH_3Cl). The others are due to collision-induced dissociation of $\text{trans-C}_2\text{H}_2\text{Cl}_2^+$ to $\text{C}_2\text{H}_2\text{Cl}^+$ and C_2H_2^+ .

exchange signal from CH_3F (IE=12.50 eV) [35] with $1,1\text{-C}_2\text{H}_2\text{Cl}_2^+$ was very weak, however. Intensities of the reagent gas ions relative to that of the incoming $1,1\text{-C}_2\text{H}_2\text{Cl}_2^+$ are plotted as a function of the reagent gas ionization energy in Figure 3 to demonstrate the difference from the $\text{trans-C}_2\text{H}_2\text{Cl}_2^+$ case. Hence it can be concluded that the recombination energy of the long-lived excited state of $1,1\text{-C}_2\text{H}_2\text{Cl}_2^+$ is slightly above 12.0 eV while those of trans- and $\text{cis-C}_2\text{H}_2\text{Cl}_2^+$ are close to or slightly below 12.0 eV.

Analysis

In view of the above experimental results, information on the excited electronic states of the three isomers of dichloroethylene cations up to the recombination energy of ~ 13 eV, or states ~ 3 eV above the ground state of each isomer, is needed to identify the long-lived excited state(s) observed. Two kinds of electronic states may be present in this range for a molecular cation, namely hole states generated by removal of an electron from an occupied orbital of the neutral and states with an electron in an orbital unoccupied in the neutral. Information on the former states is available from the photoelectron spectrum. The latter states, which may be loosely called LUMO states, can be populated by a two electron process in EI. We calculated the energies of the

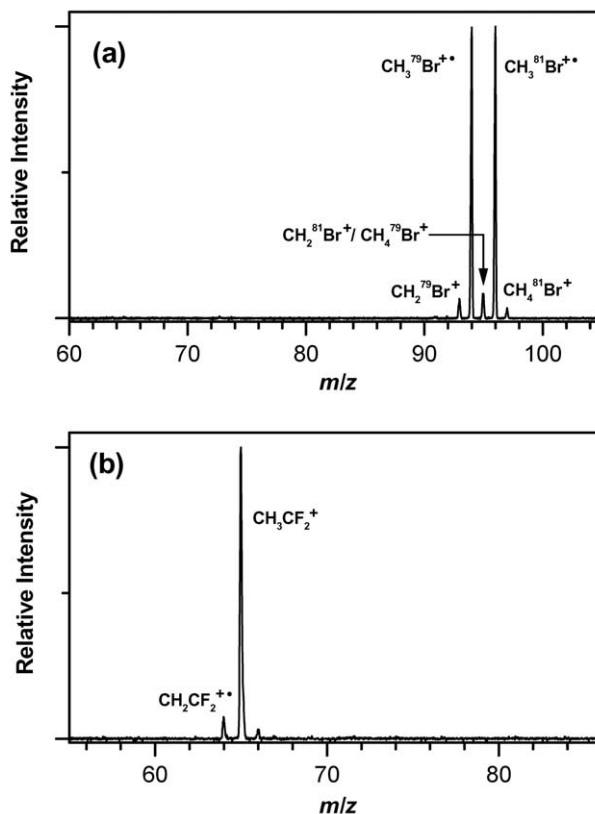


Figure 5. eV_C double focusing spectra of $\text{cis-C}_2\text{H}_2\text{Cl}_2^+$ generated by 17 eV EI with (a) CH_3Br and (b) CH_3CClF_2 in the first cell. V_S and V_C were 4070 and 4005 V, respectively. All the peaks are due to Type III ions.

lowest lying doublet and quartet LUMO states by the time-dependent density functional theory (TDDFT) at the UB3LYP level using the 6-31G** basis set. The vertical energies to the doublet states from the ground states were 4.80, 4.91, and 5.39 eV for the trans- , cis- , and $1,1\text{-C}_2\text{H}_2\text{Cl}_2^+$, respectively, while 4.89, 5.18, and 5.07 eV, respectively, were obtained for the quartet states. Hence, accepting the TDDFT/B3LYP results that are known to predict the excited state energies rather well, only low-lying hole states appearing in the photoelectron spectra need to be considered to identify the long-lived states observed. Photoelectron spectra of the three isomers of dichloroethylene were reported by several investigators [36–41]. Even though there are some minor differences, excellent agreement in the major aspects among these reports can be seen, such as the vertical ionization energies to the hole states of the cations appearing in the spectra. We will take the spectral data compiled by Kimura and coworkers [36] as the references with some corrections which will be explained later.

Considering only valence molecular orbitals, the electron configuration corresponding to the ground state of the $\text{trans-C}_2\text{H}_2\text{Cl}_2$ neutral is $(2b_g)^2(8b_u)^2(10a_g)^2(4a_u)^2$ with the orbital designations given by Kimura and coworkers. Here $4a_u$ is mostly the π orbital of the

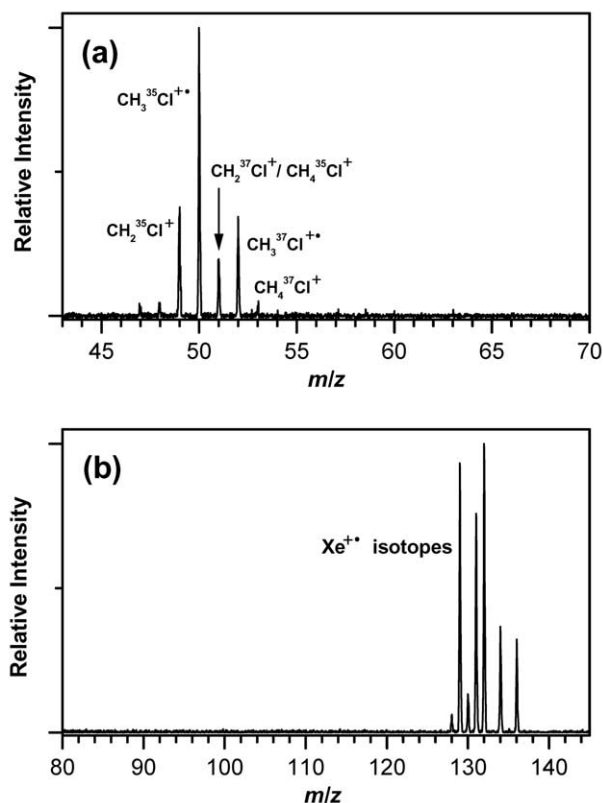


Figure 6. eV_C double focusing spectra of 1,1-C₂H₂Cl₂⁺ generated by 17 eV EI with (a) CH₃Cl and (b) Xe in the first cell. V_S and V_C were 4070 and 4005 V, respectively. All the peaks are due to Type III ions.

C–C bond with some out-of-plane chlorine nonbonding character, or $\pi(C-C)/n(Cl3p_{||})$, $10a_g$ and $8b_u$ are mostly the in-plane chlorine nonbonding orbitals, $n(Cl3p_{||})$, and $2b_g$ is mostly $n(Cl3p_{||})$. Removal of an electron from these orbitals results in the hole states \tilde{X}^2A_u , \tilde{A}^2A_g , \tilde{B}^2B_u , and \tilde{C}^2B_g which have the vertical ionization energies of 9.81, 11.86, 11.93, and 12.61 eV, respectively, according to Kimura and coworkers. The ground state electron configuration of the cis isomer is $(2a_2)^2(10a_1)^2(9b_2)^2(3b_1)^2$ with the $3b_1$, $9b_2$, $10a_1$, and $2a_2$

orbitals having the characters similar to $4a_u$, $10a_g$, $8b_u$, and $2b_g$ of the trans isomer, respectively. The hole states for the cis cation are \tilde{X}^2B_1 , \tilde{A}^2B_2 , \tilde{B}^2A_1 , and \tilde{C}^2A_2 with the vertical ionization energies of 9.83, 11.85, 12.09, and 12.51 eV, respectively. For the 1,1-isomer, Kimura and coworkers found through a Hartree-Fock calculation using the 4-31G basis set that one of the two $n(Cl3p_{||})$ orbitals is lower in energy than the $n(Cl3p_{||})$ orbital which is comparable to $2b_g$ and $2a_2$ in the trans and cis isomers, respectively. This was confirmed by our own calculations at various higher levels suggesting $(10a_1)^2(2a_2)^2(8b_2)^2(4b_1)^2$ as the ground state electron configuration for the 1,1-neutral. The first three excited electronic states appeared vertically at 1.99 (\tilde{A}), 2.57 (\tilde{B}), and 2.74 eV (\tilde{C}) above the ground state in the TDDFT/UB3LYP/6-31G** calculation. From the photoelectron peak positions at 10.00, 11.67, 12.17, and 12.51 eV, the corresponding energy gaps are 1.67, 2.17, and 2.51 eV, respectively, in good agreement with the calculated results. The calculated \tilde{B} and \tilde{C} states had the main characters of $10a_1^{-1}$ and $2a_2^{-1}$, respectively; that is to say, the orbital ordering in 1,1-cation was $2a_2 < 10a_1$ unlike $10a_1 < 2a_2$ in the 1,1-neutral. With the reassignment, the characters of the \tilde{X} , \tilde{A} , \tilde{B} , and \tilde{C} states of the 1,1-cation become similar to the corresponding states of the cis and trans cations. Since the calculated excitation energies are slightly different than the experimental data, it will be more appropriate to use the latter values to interpret the charge exchange results. In reference [36], the vertical ionization energies to the whole states are reported, which are either the averages over the vibrational structures of the bands or the peak maxima. In contrast, the recombination energy of the cation in a particular electronic state corresponds to the adiabatic ionization energy to that state. Since the photoelectron peaks for \tilde{X} , \tilde{A} , \tilde{B} , and \tilde{C} in the reference are vibrationally resolved, we estimated their vertical ionization energies from the 0-0 positions. The results are listed in Table 2 together with the vertical ionization energies mentioned above.

If the \tilde{C} or higher excited states of trans- and cis-

Table 2. Recombination energies (eV)^a of the \tilde{X} , \tilde{A} , \tilde{B} , and \tilde{C} electronic states of the three isomers of dichloroethylene cations and the calculated radiative lifetimes (μsec)^b of the \tilde{A} and \tilde{B} states

State	Trans	Cis	1.1
\tilde{X}	9.46 (9.81)	9.54 (9.83)	9.68 (10.00)
\tilde{A}	11.67 (11.86)	11.52 (11.85)	11.55 (11.67)
\tilde{B}	11.85 (11.93)	11.86 (12.09)	12.13 (12.17)
\tilde{C}	12.46 (12.61)	12.35 (12.51)	12.47 (12.51)
Radiative lifetime	Trans	Cis	1.1
$\tilde{A} \rightarrow \tilde{X}$	180	– ^c	– ^c
$\tilde{B} \rightarrow \tilde{X}$	– ^c	220	37
$\tilde{B} \rightarrow \tilde{A}$	4.3	330	0.84

^aAdiabatic ionization energies estimated from the spectral data in ref. 36. Vertical ionization energies tabulated in the same references are shown inside the parentheses.

^bResults from the TDDFT/UB3LYP/6-31G** calculation.

^cForbidden transitions.

$C_2H_2Cl_2^+$ are long-lived, Xe (IE = 12.12 ± 0.02 eV) can be ionized efficiently by charge exchange with the cations in these states. The fact that the Xe^+ signal was extremely weak suggests that the \tilde{A} and \tilde{B} states are the only candidates for the long-lived excited states in these cases. If only the \tilde{A} states are long-lived which have recombination energies of 11.67 and 11.52 eV for the trans and cis cations, respectively, the prominent appearance of peaks originating from CH_3CClF_2 (IE = 11.98 ± 0.01 eV) can not be explained. This suggests long lifetimes for the \tilde{B} states. The reaction energies (ΔE) evaluated for the charge exchange of the \tilde{B} states with CH_3CClF_2 using data in Tables 1 and 2 are 0.13 and 0.12 eV, respectively, for the trans and cis cations, which are slightly larger than the 0.1 eV criterion established previously [24]. The slight mismatch may have been caused either by errors in the estimation of the adiabatic ionization energies of the \tilde{B} states or by an error in the ionization energy of CH_3CClF_2 reported in the literature. In the case of the 1,1-cation, inability to ionize CH_3F (IE = 12.50 eV) indicates that the \tilde{C} or higher states decay or dissociate rapidly. On the other hand, the prominent charge exchange signal from Xe (IE = 12.12 ± 0.02 eV) indicates a long lifetime of the \tilde{B} state (RE = 12.13 eV). It is interesting to note that the \tilde{B} states of the cations of all three isomers are long-lived. These states are generated by removal of an electron from an in-plane nonbonding orbital of chlorine. The \tilde{A} states of the cations are formed by removal of an electron from the other in-plane nonbonding orbitals. Whether they would have a long lifetime or not can not be determined by the present charge exchange technique.

The fact that an excited electronic state has a long lifetime means that its decay to lower states, either by radiative or by radiationless process, is rather slow. Theoretical calculation of the radiationless decay, or internal conversion in the present case, is rather difficult. However, radiative lifetimes can be evaluated from the oscillator strengths obtained from a TDDFT/UB3LYP/6-31G** calculation. The $\tilde{A} \rightarrow \tilde{X}$ transitions in the cis and 1,1-cations are optically forbidden. Even though the similar transition is optically allowed for the trans cation, the calculated radiative lifetime is as long as 180 μs ; that is to say, based on the radiative lifetime alone, there is a possibility that the \tilde{A} state of cations of all three isomers are long-lived. The radiative $\tilde{B} \rightarrow \tilde{X}$ transitions are not efficient either, being dipole forbidden for the trans cations and having the calculated lifetimes of 220 and 37 μs for the cis and 1,1-cations, respectively. Since the $\tilde{B} \rightarrow \tilde{A}$ transitions can affect the lifetimes of the \tilde{B} states, we also checked radiative lifetimes for these transitions. These were 4.3, 330, and 0.84 μs for the trans, cis, and 1,1-isomers, respectively. The results for the trans and 1,1-isomers are incompatible with the experimental results. These values obtained for the transitions between two excited states can be erroneous, however, especially because minor energy errors for the two close-lying states can lead to large errors in the radiative lifetimes.

Conclusions

Detection of ions from various reagent gases with different ionization energies by charge exchange has shown that an electronic state(s) lying ~ 2 eV above the ground states of trans-, cis-, and 1,1- $C_2H_2Cl_2^+$ are long-lived when ions are generated by 17 eV EI. There are two electronic states of the cations in this energy range, \tilde{A} and \tilde{B} , both of which are formed by removal of an electron from the chlorine nonbonding orbitals of the neutrals. Results from the charge exchange with Xe indicate that the \tilde{B} states are long-lived. Whether the \tilde{A} states are also long-lived or not can not be determined by the present experiments. Since the \tilde{A} and \tilde{B} states are very close in energy, there is a possibility that these states interconvert freely. As far as they do not undergo rapid relaxation to the ground states, this model is also compatible with the experimental results. Finding long-lived states in cations with mixed halogen substitution will be useful to establish the general validity of the correlation that an ionic state generated by removal of an electron from an in-plane orbital of a neutral can have a very long lifetime.

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