# Unimolecular Dissociation Dynamics of Vinyl Chloride on the Ground Potential Energy Surface: The Method of Excitation and Product State Distributions of HCl and Cl Fragments[†]

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The unimolecular dissociation dynamics of vinyl chloride on the ground electronic potential energy surface have been investigated. The vibrationally excited vinyl chloride in its ground electronic state is prepared using the isomerization process of α-chloroethylidene radical to vinyl chloride via the hydrogen atom migration, where the chloroethylidene radical is produced by the ultraviolet photolysis of 3-methyl-3-chlorodiazirine. The vinyl chloride molecule formed in this excitation scheme is highly vibrationally excited in its ground electronic state due to the bond formation between two carbon atoms, and undergoes unimolecular reactions of HCl elimination or C−Cl bond fission. The rotational and vibrational state distributions of the HCl fragments and the spin−orbit state branching ratio of the Cl atoms have been measured with a resonantly enhanced multiphoton ionization (REMPI)/time-of-flight mass spectrometry. The overall state distributions of the HCl and Cl fragments are much colder than those in the 193 nm photodissociation. The rotational distributions of the HCl($v = 0$) and HCl($v = 1$) fragments fit to the Boltzmann distributions at $T_{\mathrm{rot}} = 470$ and 130 K, respectively. The vibrational branching ratio of HCl($v = 1$)/HCl($v = 0$) and the spin−orbit state branching ratio of Cl*($^2P_{1/2}$)/Cl($^2P_{3/2}$) are measured to be 0.15 ± 0.03 and 0.15 ± 0.02, respectively. The differences in the dynamical observations of vinychloride produced by this excitation scheme and the 193 nm photoexcitation are interpreted in terms of the large difference of excitation energies between two excitation schemes.

## I. Introduction

Photodissociation dynamics of vinyl chloride (VC) have been investigated for many years by several research groups. In the 1970's, the mechanisms of HCl elimination reaction in the flash photolysis at ∼200 nm have been revealed by the photochemical laser studies by Berry[1] and the detailed product analyses by the Wijnen's group.[2−6] With the advance of laser technology, more detailed studies on the photodissociation of VC have been carried out. These include the infrared emission measurement by McDonald's group,[7] the measurement of translational energies of HCl and Cl fragments formed in the photodissociation at 193 nm by Umemoto et al.[8] Recently, Gordon's group has reported an extensive series of works on the photodissociation of VC and other chloroethylenes at 193 nm.[9−15] They have measured the rotational energy contents of the HCl frgments,[9,10] the Cl*/ Cl branching ratio,[9] the translational energy distributions[11,12] of HCl and Cl, and the rovibrational and translational energy distributions of $H_2$.[13] More recently, Blank et al.[16] reinvestigated the vinyl chloride photodissociation at 193 nm by using the synchrotron vacuum UV source and photofragment translational spectroscopy, confirming the previous observations by other groups and identified some secondary dissociation channels of the radical fragments.

These studies have revealed the detailed mechanisms of photodissociation of VC at 193 nm. Absorption of a 193 nm photon corresponds to the $\pi^*-\pi$ transition which has a large oscillator strength at this wavelength. The VC molecules excited to the $\pi^*$ state do not decompose directly, rather they relax to the lower excited states or to the ground state.[8,16] With the exception of the Cl fragments which come from both $\sigma^*$ and ground states, all other fragments are known to come from the unimolecular decomposition in the ground electronic state.[8,16] In addition, the three-center elimination is found to be the major contributor to the HCl and $H_2$ fragments formation[10,13] in contrast to the conclusion of the chemical laser studies,[1,17] in which the four-center reaction was suggested to be dominant. The rotational distributions of HCl fragments revealed an interesting feature that the $v = 0$ fragments show a non-Boltzmann distribution whereas the $v > 0$ fragments follow Boltzmann-like behavior.[9,10] This result has been explained in terms of a conjecture that a significant amount of energy goes into the translational and rotational degrees of freedom of HCl fragments during the subsequent isomerization of vinylidene to acetylene since the isomerization process is so rapid that it occurs before complete separation of two fragments, HCl and vinylidene.[15]

Reihl and Morokuma calculated barrier heights and asymptotic energies for various reaction channels of the vibrationally hot VC on the ground potential energy surface using ab initio molecular orbital methods.[18] The barrier for the three-center elimination of HCl is predicted to be lower than that for the four-center pathway in accordance with the observation of the Gordon's group. Since the barrier to H-atom migration in VC was found to be slightly lower than the 3-center HCl elimination, they suggested that H-atom migration may take place before dissociation. Although the predictions of the ab initio molecular orbital study[18] by Reihl and Morokuma have frequently been

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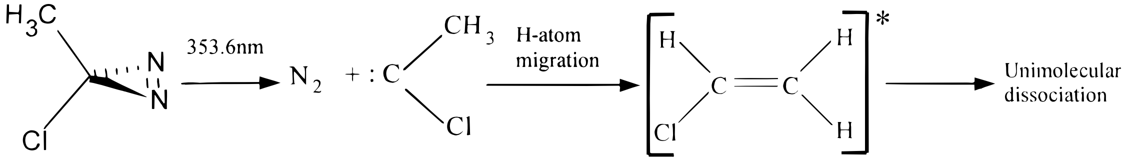
**SCHEME 1**



borrowed to interpret the experimental results of the 193 nm photodissociation of VC, the theoretical study itself was on the unimolecular dissociation of the vibrationally excited VC molecules in its ground electronic state. Absorption of an 193 nm photon could reach several excited states of VC such as $\pi^*$, $\sigma^*$, or 3s Rydberg states at the same time,[8] and thus the dissociation processes might be complicated by the coupling of these excited states and the ground electronic state.

We devised a new excitation scheme for preparing VC molecules in highly vibrationally excited levels in the ground electronic state. In this excitation scheme, the vibrationally hot VC molecule in the ground state is formed by the H-atom migration in the carbene radical which is produced by the photodecomposition of 3-methyl-3-chlorodiazirine (MCD), as summarized in Scheme 1.

Formation of various carbenes in the photodecomposition of substituted diazirines has been known[19] for a long time although those radicals are reported to be trapped only recently.[20] It is well-known that the carbenes with a $\beta$-H-atom isomerize to ethylenes very rapidly due to the low barrier to the H-atom migration.[19-22] More important is that the H-atom migration releases ~55 kcal/mol of energy[18] as the vibrational energy to the product molecule in the ground electronic state. Photolysis of 3-chloro-3-methyldiazirine produces the α-chloroethylidene which subsequently isomerizes to vinyl chloride, having enough energy to undergo further unimolecular dissociation on the ground potential energy surface.[23,24] (Scheme 1)

In this paper, we report an application of Scheme 1 as the excitation method for unimolecular dissociation dynamics study on VC. It is demonstrated that Scheme 1 generates highly vibrationally excited VC decomposing on the ground potential energy surface to produce HCl or Cl. The HCl rovibrational state distribution and the $Cl^*(^2P_{1/2})/Cl(^2P_{3/2})$ branching ratio have been measured. Our results show some unique features different from those obtained at the 193 nm photodissociation.

## 2. Experimental Section

The experiment was performed for the cooled sample in a skimmed molecular beam using the conventional resonantly enhanced multiphoton ionization(REMPI)/time-of-flight mass spectrometry. The ~5% MCD mixture in He, kept at the pressure of 1 atm, was expanded through a 0.5 mm diameter nozzle, which was driven with a homemade driver. At the 30 mm distance from the nozzle, an 1.0 mm diameter skimmer was placed to separate the source and ionization chambers. The photolysis laser light was generated in a KD*P crystal by second-harmonic generation of the visible output of a pulsed dye laser (Lambda Physik SCANmate 2) pumped with a Q-switched Nd:YAG laser (Spectra-Physics GCR-11). The photolysis laser beam was separated from the visible light and directed to the interaction zone located at the center of the extraction electrodes of the time-of-flight mass spectrometer. The photolysis laser wavelength was fixed at 353.6 nm, which corresponds to the origin band of the $S_1-S_0$ transition of the MCD[25] cooled in a supersonic jet (See Figure 1). The pulse energy of the photolysis laser was 2−3 mJ/pulse and the beam size was ~3 mm in diameter at the interaction zone. About 50 ns later, the probe laser pulse (~1 mJ/pulse), which was generated by frequency-doubling of the blue output (Coumarin 480) from the second dye laser (Lambda Physik SCANmate 2) pumped with a Q-switched Nd:YAG laser (Spectra-Physics GCR-150), counterpropagated the photolysis laser beam. The probe laser beam was focused to the interaction zone with a 50 cm focal length quartz lens.

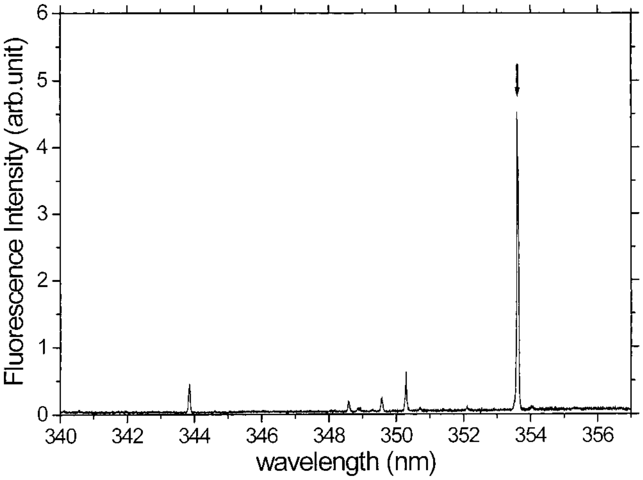


**Figure 1.** Fluorescence excitation of 3-methyl-3-chlorodiazirine cooled in supersonic jet. The peak marked with an arrow is the origin band at which the photolysis laser wavelength was fixed for further experiments.

The HCl and Cl fragments were ionized with the (2 + 1) REMPI process using the $F^1\Delta$ Rydberg state and $^2D_{3/2}$ state, respectively,[26] as the intermediate levels and then the $HCl^+$ and $Cl^+$ ions were extracted and accelerated to a microchannel plate detector. The detector signal was amplified by 5 times in a preamplifier (SRS SR245) and processed with a gated integrator (SRS SR250) interfaced to a personal computer. Only the $H^{35}Cl^+$ and $^{35}Cl^+$ ion signals were processed. The $HCl^+$ and $Cl^+$ ion signal intensities did not change noticeably when the delay between the photolysis and probe pulses was varied from 10 to 500 ns. Thus, the delay was fixed at 50 ns for all subsequent measurements. Rotation of the polarization of the photolysis or probe laser beams did not change the signal intensity noticeably. The shot-to-shot fluctuation of the probe laser pulses was monitored with a pyroelectric joulemeter (Molectron J3−05) to normalize the REMPI signal.

The 3-methyl-3-chlorodiairine (MCD) sample was prepared following the procedure described by Graham.[27] The gaseous MCD sample synthesized was collected in a 4 L stainless steel cylinder and mixed with He. Since many diazirines are known to be explosive during phase transitions, no trap-to-trap distillation was tried to avoid the possible explosion. Since the MCD sample in the stainless steel cylinder was found to decompose slowly, the fresh sample mixture was prepared every week.

## 3. Results

**3-1. Generation of Vibrationally Hot VC and Identification of Dissociation Products**. To find the wavelength of the

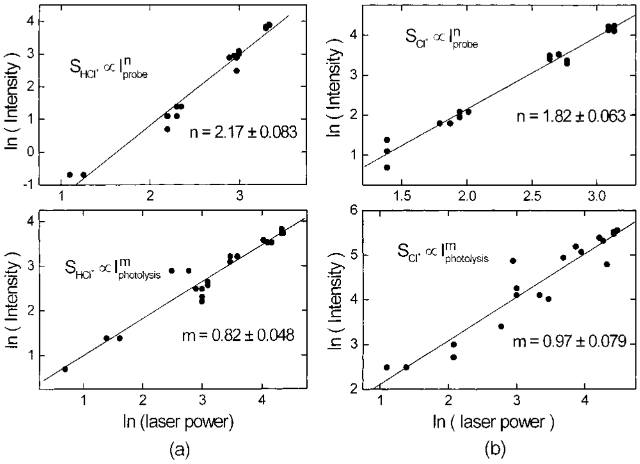


**Figure 2.** Photolysis and probe laser power dependence of the (2 + 1) REMPI signals for the (a) HCl and (b) Cl fragments.

photolysis laser, the fluorescence excitation spectrum of MCD was taken in a free jet expansion and is shown in Figure 1. These absorption bands correspond to the $S_1-S_0$ ($\pi^*-n$) transition.[25] The decrease of band intensity toward higher frequency, which is very different from the intensity distribution of the absorption spectrum[25] of the gaseous sample at room temperature, is due to a rapidly increasing rate of dissociation rate over the small barrier on the $S_1$ surface with increasing energy.[21,28] We chose the transition wavelength of the origin band at 353.6 nm as the photolysis laser wavelength, which was used throughout this work. The measured fluorescence lifetime of the origin band was limited by the pulse duration (~5 ns) of our excitation laser and the PMT response time, suggesting that the excited MCD to the $S_1$ state decays within less than a few nanoseconds.

When both the photolysis and probe lasers were on, the mass signals corresponding to $HCl^+$ and $Cl^+$ ions were observed. Since the HCl and Cl fragments may also be formed from MCD or the primary photolysis products by various multiphoton absorption of the various combination of photolysis and probe lasers, the power dependence of the ion signal intensity on the photolysis and probe lasers was measured. As shown in Figure 2, both $HCl^+$ and $Cl^+$ ion signals show linear and quadratic dependence on the photolysis and probe laser power, respectively, confirming that those ion signals are for the HCl and Cl fragments produced by Scheme 1. The secondary photolysis of α-chloroethylidene radical by the photolysis laser pulse may yield Cl atoms. If this is the case or there is a nonnegligible contribution of this mechanism, the $Cl^+$ signal would give the quadratic dependence on the photolysis laser power or at least a significant deviation from the linear dependence, which is not in accord with what we observed. Absorption of a probe laser photon by the vibrationally hot VC may lead to the generation of HCl and Cl fragments, but in this case both ion signals should show a third-power dependence on the probe laser. Hence, it is concluded that the observed HCl and Cl fragments are the primary products of unimolecular dissociation of the vibrationally excited VC prepared by Scheme 1.

If the transitions are partially saturated, the power dependence measurement itself is not enough to distinguish the possible mechanisms. Let us consider two possible cases; the hot VC absorbs one more photon of the photolysis laser or absorbs a photon of the probe laser pulse. The absorption of the VC begins at about 220 nm and reaches the maximum near 184 nm. Since the photolysis laser wavelength was fixed at 353.6 nm in this work, it does not seem reasonable that these VC molecules absorb a photon at such a long wavelength, even though the VC molecules prepared in this work are vibrationally hot. The vibrationally hot VC molecules may absorb the probe laser light at about 240 nm. If the vibrationally hot VC absorbs a photon of the probe laser at near 240 nm, however, the excited VC molecule must have an internal energy of at least 174 kcal/mol. This amount of internal energy is even larger than that of 193 nm excitation and thus the energy contents among the fragments such as HCl and Cl should be larger than those of the 193 nm photolysis, which is in contradiction to our results (vide infra).This discussion along with the measured laser power dependences indicates that the possibility of additional photon absorption of the vibrationally hot VC prepared by photolysis of MCD is negligible for both of the photolysis and probe lasers.

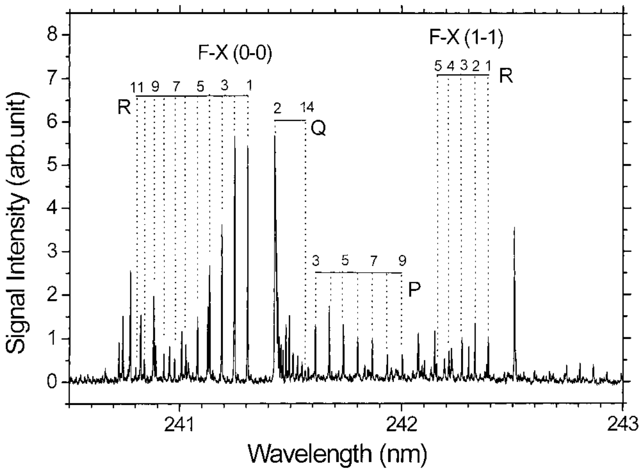


**Figure 3.** (2 + 1) REMPI spectrum of HCl produced from vinyl chloride excited by Scheme with the corresponding rovibronic assignments. The relatively weak intensity of the F-X(1-1) band compared to the F-X(0-0) band indicates that the HC($v = 1$) fragments are minor. The unassigned peaks around the R-branch of the F-X(0-0) band belong to the g-X(0-0) band and the S-branch of the F-X(0-0) band.[29]

**3-2. Rovibrational State Distributions of the HCl Fragments**. The (2 + 1) REMPI spectrum of the HCl fragments is shown in Figure 3 with the rovibrational assignments. Several unassigned peaks around the R-branch of the F-X(0-0) band were known to belong to the g-X(0-0) band and the S-branch of the F-X(0-0) band.[29] Since the fraction of the HCl($v = 1$) products was small compared to the HCl($v = 0$) products, the F-X(0-1) band was not observed with reasonable signal-to-noise ratio for further analysis. The rotational populations of the HCl($v = 0,1$) fragments were measured from the corresponding peak intensities and the correction factors[30] of each rovibrational transition lines. The correction factors are introduced to correct the intensity anomaly due to the perturbation of the F state.[31] The final rotational distributions were obtained by averaging at least three measurements for each band.

The Boltzmann plots of the rotational populations of the HCl($v = 0$) and HCl($v = 1$) are given in Figures 4 and 5, respectively. As shown in Figures 4 and 5, the rotational distributions of the HCl($v = 0$) and HCl($v = 1$) fragments show Boltzmann-like behavior, and a least-squares fit gives the rotational temperatures $T_R = 470 \pm 20$ K for $v = 0$ and $T_R = 130 \pm 25$ K for $v = 1$ HCl, respectively. The population ratio of the HCl($v = 1$)/($v = 0$) is difficult to measure quantitatively because the relative intensity of the F-X (0-0) and (1-1) bands are not reported for all rotational transition lines.[30] Thus the vibrational branching ratio ($v = 1$)/($v = 0$) is roughly estimated from the correction factors[30] for the R(1) lines for the F-X (0-0) and (1-1) bands and the rotational temperatures obtained from

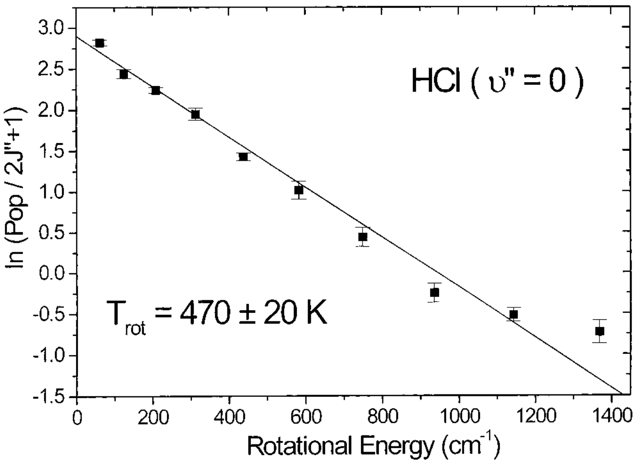


**Figure 4.** Rotational state distribution of HCl($v$ = 0). The straight line is the least-squares fit to a Boltzmann distribution of the rotational temperature of 470 ± 20 K. Error bars are single standard deviations.

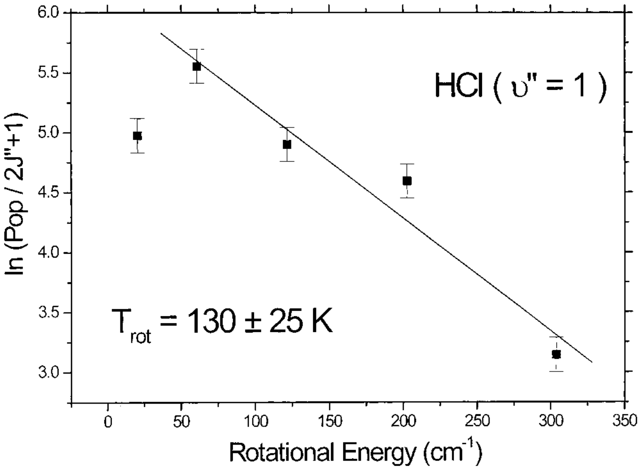


**Figure 5.** Rotational state distribution of HCl($v$ = 1). The straight line is the least-squares fit to a Boltzmann distribution of the rotational temperature of 130 ± 25 K. The $J = 1$ level was not included in the fitting. The number of data points is limited because of the weak intensity of the F-X(1-1) band and overlap of the transition lines.

the least-squares fit. The branching ratio ($v$ = 1)/($v$ = 0) is determined to be 0.15 ± 0.03.

**3-3. The Spin−Orbit State Branching Ratio of Cl**. A (2 + 1) REMPI spectrum of the Cl($^2P_{1/2}$) and Cl($^2P_{3/2}$) atoms is shown in Figure 6. It demonstrates that the Cl atoms are produced in both the ground and excited spin−orbit states in the dissociation of the vibrationally excited VC. Since a small amount of $Cl^+$ ions was found to be produced without the photolysis laser pulse, the spectrum in Figure 6 was obtained by subtracting the spectrum obtained with the probe laser alone from that obtained with both the photolysis and probe lasers. The branching ratio of Cl($^2P_{1/2}$) with respect to Cl($^2P_{3/2}$) is measured to be 0.15 ± 0.02 from the integrated peak areas corrected for the relative REMPI efficiencies of 2.5 ± 0.1 for the $^2D_{3/2} \leftarrow {}^2P_{1/2}$ and $^2D_{3/2} \leftarrow {}^2P_{3/2}$ transition lines.[32]

## 4. Discussion

**4-1. The Method of Excitation**. It is successfully demonstrated in this work that the $\beta$-H migration in α-chloroethylidene radical prepares the vibrationally excited VC in its ground electronic state. Since the H-atom migration releases a large amount of energy, the VC molecules excited by Scheme 1 undergo unimolecular dissociation producing HCl and Cl fragments.

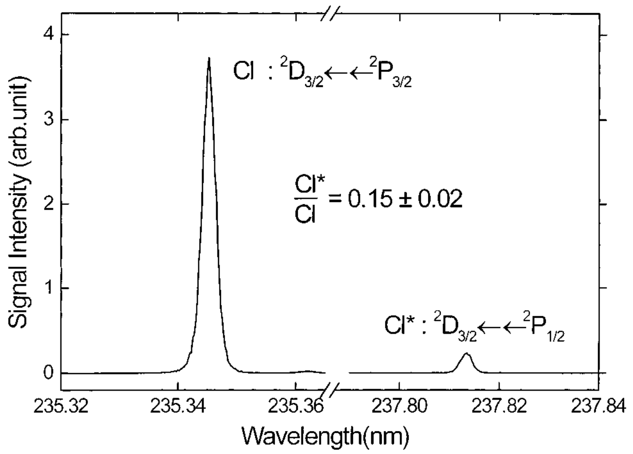


**Figure 6.** (2 + 1) REMPI spectra of the Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) products. The branching ratio of Cl($^2P_{1/2}$)/($^2P_{3/2}$) and was estimated from the areas of the peaks and the relative REMPI efficiencies of 2.5 ± 0.1 for the $^2D_{3/2} \longleftarrow {}^2P_{1/2}$ and $^2D_{3/2} \longleftarrow {}^2P_{3/2}$ transition lines.[32]

This work suggests that the $\beta$-H-atom migration in carbenes can be used as an efficient method to vibrationally excite ethylene and its derivatives in their ground electronic states. The main advantage of using Scheme 1 is that the energy region, which is not accessible by direct optical transition, can be reached. VC has no absorption at wavelengths longer than 200 nm, and thus it is impossible to directly excite the VC molecule at the energies near the barrier for HCl elimination, ~70 kcal/mol. That may be the main reason the direct optical excitation at 193 nm has been employed in most of other photodissociation studies on various ethylenes. Since an 193 nm photon corresponds to 148 kcal/mol which is far above the barriers for various dissociation channels of VC,[18] the detailed dynamics at energies near the barriers were not directly observed. Excitation via Scheme 1, however, can prepare the VC molecules with much lower energy (vide infra) than 193 nm excitation, and thus may reveal the dynamical phemomena which were not observed in the previous studies. In addition, since no electronically excited state is involved in the excitation by Scheme 1, the observed dynamics are purely for the ground state. Although this excitation method has some merits over direct optical excitation, it has also drawbacks for dissociation dynamics studies. Since the ethylidene radicals are produced by photodissociation, the energy content among the ethylidene radicals is not mono-energetic, but distributed over a certain range. The broad distribution of energy in reacting molecules smears out the state-to-state dynamical phenomena. And the energy content among the reacting molecules cannot be tuned precisely in contrast to the optical excitation. Hence the excitation by Scheme 1 and subsequent dynamical studies may augment the direct optical excitation for detailed understanding of dissociation dynamics of various ethylenes.

In addition to diazirines used in this work, ketenes are also candidates of precursors for the photochemical generation of carbenes with $\beta$-H-atoms, as shown in Scheme 2 for generation of VC.

Ketenes have relatively weaker absorption than diazirines in the near-ultraviolet region but the energy content among the excited molecules can be better defined than for diazirines since the potential energy surface for singlet carbene generation from ketenes is known to have no reverse barrier.[33,34]

**4-2. The Internal Energy Content of the Vibrationally Excited VC**. In the dissociation dynamics studies, the energy content of the reacting molecules is one of the most important

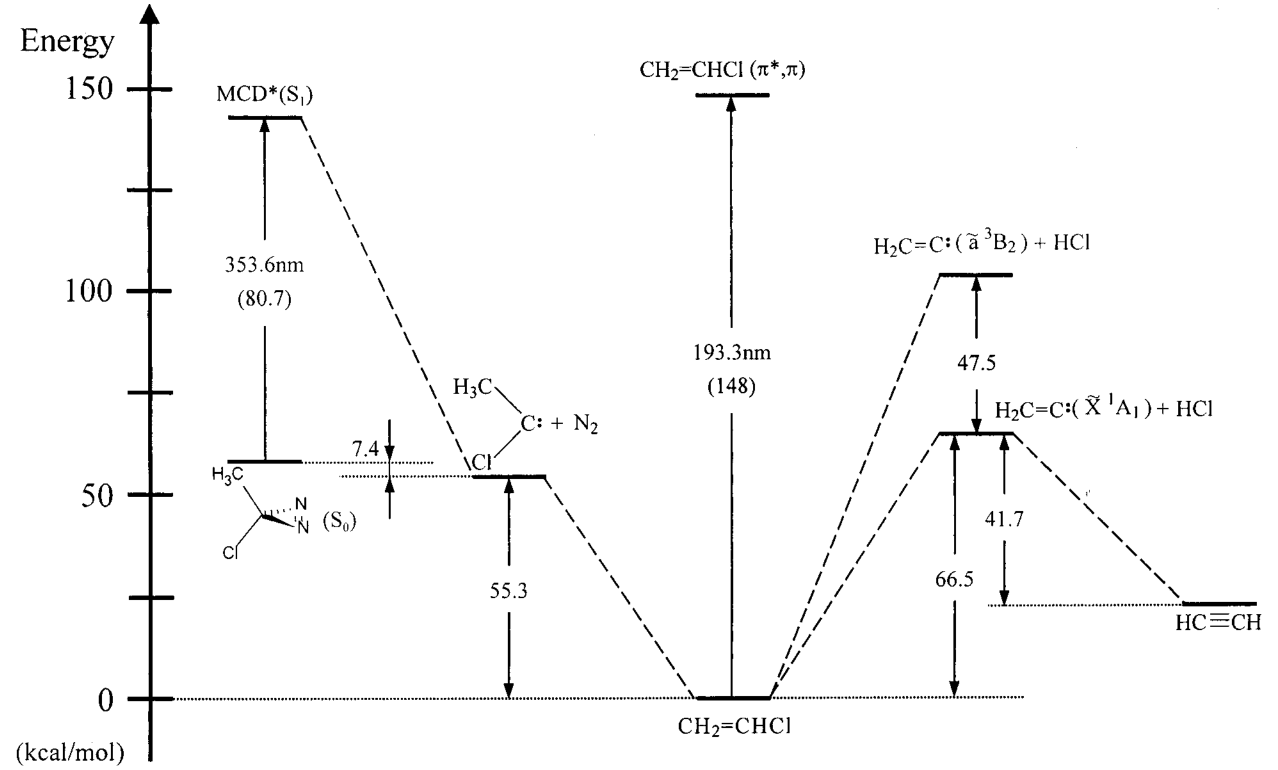
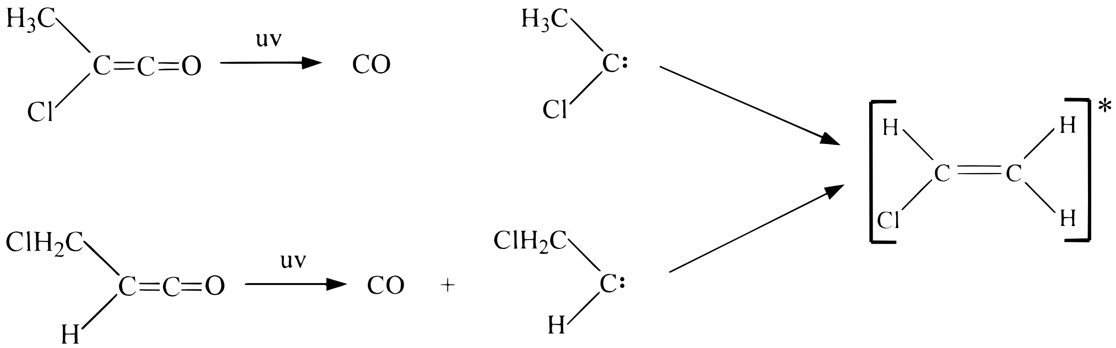


**Figure 7.** Schematic energy level diagram of the species involved in dissociation of 3-methyl-3-chlorodiazirine (MCD) and vinyl chloride. The energy of vinyl chloride is set to zero and the barriers for reactions are not shown. Barrier to production of the HCl($X^1\Sigma^+$) and $H_2C{=}C$: ($^3B_2$) is too high to be accessed by the vinyl chloride molecules excited by Scheme 1. The energy differences are given in the unit of kcal/mol.

**SCHEME 2**



parameters to understand and interpret the experimental observations. As stated above, the energy of the VC molecules excited by Scheme 1 cannot be determined accurately because the excess energy of the photolysis of MCD is distributed over all degrees of freedoms of the products, α-chloroethylidene and $N_2$. However, the energy content can be estimated from the thermochemical data of MCD[35] and α-chloroethylidene[36] and the dissociation dynamics of MCD. According to the calculation by Riehl and Morokuma, the energy difference of the α-chloroethylidene and VC in their ground states is 55.3 kcal/mol, and the barrier for the H-atom migration of α-chloroethylidene to VC is 13.5 kcal/mol.[18] It means that the VC molecules prepared by Scheme 1 have the internal energy of at least 68.8 kcal/mol. They also predicted the barrier for the C−Cl bond fission of VC to be 89.8 kcal/mol.[18] Since Cl atoms are observed in our experiment, some of the VC molecules must have internal energies more than 89.8 kcal/mol. Although the exact branching ratio of the HCl/Cl has not been measured in this work, the C−Cl fission seems to be a minor channel from the fact that the (2 + 1) REMPI signals of the HCl and Cl products have comparable intensities and the Cl atoms must have higher ionization efficiency and smaller number of quantum states than the HCl molecules. The small yield of Cl indicates that most of the vinyl chloride molecules produced by Scheme 1 have lower energies than the threshold of the C−Cl bond fission, 89.8 kcal/mol. Considering the lower and upper bounds, the average energy of the VC molecules formed by Scheme 1 is estimated to be 80 kcal/mol, but with a large error bound of ±10 kcal/mol.

The average internal energy of 80 kcal/mol of VC is somewhat smaller than the expectation considering the large excess energy of the dissociation of MCD to $N_2$ + α-chloroethylidene. From the heat of formations of the MCD[23] and the α-chloroethylidene,[35] 58.1 and 50.7 kcal/mol, respectively, and considering the energy of a 353.6 nm photon, the available energy to be distributed over all degrees of freedoms of $N_2$ and α-chloroethylidene fragments is 88 kcal/mol (Figure 7). Among the 88 kcal/mol of energy, 13.5 kcal/mol has to be saved as the internal energy of the α-chloroethylidene molecule in order for the α-chloroethylidene molecule to overcome the barrier to isomerization to VC. Thus the net available energy to be distributed to $N_2$ + α-chloroethylidene fragments is 74.6 kcal/

mol. Our preliminary result[36] of the rotational and translational energy distributions of the $N_2$ fragments produced in the 353.6 nm photodissociation of MCD showed that $N_2$ fragments are highly rotationally excited (~60) and also translationally hot, suggesting that most of the available energy goes to the translational energies of two fragments and rotational energy of $N_2$ fragment. Hence our estimation of ~80 kcal/mol for the internal energy of VC, resulting from that only a small fraction of the available energy goes into α-chloroethylidene does not seem unreasonable.

**4-3. State Distributions of the HCl and Cl Fragments**. As shown in Figures 4 and 5, the rotational distributions of the HCl($v = 0$) and ($v = 1$) fragments are well described by Boltzmann plots at rotational temperatures of 470 K for $v = 0$ and 130 K for $v = 1$, respectively. The colder HCl rotational state distributions compared to those obtained in the 193 nm photodissociation can be understood qualitatively in terms of the smaller available energy of the fragments produced from the vibrationally excited VC in this work. An interesting feature of our rotational distributions though is that the Boltzmann plot of the rotational distribution of HCl($v = 0$) fits to a single rotational temperature in contrast to what observed in 193 nm photodissociation.[9,10]

The rotational distribution of HCl($v = 0$) from the 193 photodissociation of VC[9] was fit with two rotational temperatures of 340 and 22600 K, while those of vibrationally excited HCl fragments were fit with the rotational temperature of 2100 K for $v = 1$ and 1800 K for $v = 2$, respectively. The non-Boltzmann rotational distributions of HCl($v = 0$) fragments have also been observed in the 193 nm photodissociations of vinyl chloride-$d_1$[10] and *cis*, *trans*, and 1,1-dichloroethylenes.[14] Interestingly, 2-chloro-1,1-difluoroethylene, of which the product is the $F_2C{=}C\colon$ radical having a high barrier for its isomerization to $FC{\equiv}CF$, was found to show a single rotational temperature of 4200 K for HCl($v = 0$).[15] From these results, Gordon and co-workers concluded that the high rotational-temperature HCl($v = 0$) fragments are formed because a part of the large amount of energy released during the subsequent isomerization of vinylidene to acetylene goes into the translational and rotational degrees of freedom of HCl fragments.[15] They suggested that the isomerization process is too rapid, and it occurs before the fragments separate completely. The single rotational temperature for vibrationally excited HCl($v > 0$) has been explained in terms of the vibrational adiabaticity.[10]

According to the model proposed by Gordon and co-workers, the rotational distribution of HCl($v = 0$) produced from Scheme 1 is expected to be very hot because a large amount of energy is released by the isomerization of the counter fragment, vinylidene, to acetylene. It seems that this discrepancy originates from the large difference of the excitation energies of our excitation scheme and 193 nm photoexcitation. That is, the vinylidene radicals produced from the VC molecules excited by Scheme 1 do not have enough energy to rapidly isomerize to acetylene. As a result, the isomerization occurs only after complete separation of the HCl and vinylidene fragments and thus the excess energy released during isomerization cannot go into the rotational degree of freedom of HCl. In the 193 nm photoexcitation case, however, the vinylidene radicals are so energetic to initiate the isomerization process even before the complete separation of the HCl and vinylidene fragments along the reaction coordinate. This conjecture also explains why the vibrationally excited HCl($v>0$) products show the much colder rotational distributions compared to HCl($v = 0$) in the 193 nm photoexcitation.[9,10,14,15] Since the vibrational energy of the HCl($v > 0$) fragments has to be adiabatically fixed during the dissociation process, the counter fragments, vinylidene radicals have the less energy and thus it take more time for those associated with HCl($v > 0$) to isomerize into acetylene. As expected from this model, the rotational temperatures of HCl($v = 1$) formed in the 193 nm photodissociation of VC, 2-chloro-1,1-difluoroethylene, 1,1-dichloroethylene, and *cis*- and *trans*-dichloroethylenes were 2100, 3400, 1290, and 1390 K, respectively, which are much lower than those of HCl($v = 0$).[9,10,14,15] And thus the rotational temperature of 470 K of HCl($v = 0$) from Scheme 1 is consistent with the previous results considering the much smaller excitation energy of VC than that given in the 193 nm photoexcitation.

Now it is required to explain why the colder component, which was observed in 193 nm photodissociation, does not appear in our work. Interestingly, Gordon and co-workers did not provide a reasonable explanation on the origin of the low-temperature component of the rotational distribution of the HCl fragments. It seems to us that the rotational temperature of 340 K is too low for the fragments formed on the ground PES following 193 nm photoexcitation of VC since the energy of an 193 photon is almost 80 kcal/mol higher than the barrier for three-center HCl elimination. We speculate that the cold component might be produced along an excited electronic state leading to the HCl($X^1\Sigma^+$) and electronically excited vinylidene. In this case, the HCl fragments will have the less translational energy compared to those formed on the ground electronic states. The experimental results of Gordon and co-workers support our speculation. The kinetic energy measurement of the HCl fragment produced in the 193 nm photodissociation of VC by Huang et al. showed that the low J HCl($v = 0$) fragments were found to have a much higher probability near the zero kinetic energy than the higher J HCl($v = 0$) products.[11] In contrast, the kinetic energy distributions of the $v = 1$ and 2 HCl fragments are nearly the same for all rotational levels measured.[11] This observation indicates that some of the low J HCl observed in the 193 nm photodissociation have a small average kinetic energy which is expected for a dissociation channel with a higher barrier than that of the three-center HCl elimination on the ground PES. A possible path is the dissociation to HCl($X^1\Sigma^+$) and $H_2C{=}C\colon$ ($^3B_2$), which was observed by Fahr and Laufer in the VUV photolysis of VC.[37] The $a^3B_2$ state of vinylidene was measured to be located 47.5 kcal/mol above the $X^1A_1$ state.[38] It suggests that the lower bound of the barrier height for dissociation to HCl($X^1\Sigma^+$) and $H_2C{=}C\colon$ ($^3B_2$) is 114 kcal/mol. Since this barrier is far above the average internal energy of VC prepared by Scheme 1, it is believed that the excited PES leading to $H_2C{=}C\colon$ ($^3B_2$) is not accessible in our excitation scheme and thus the cold component is not observed in this work.

The relative yield of ($v = 1$)/($v = 0$) of HCl produced by Scheme 1 was estimated to be 0.15 ± 0.03. Since the relative yield of the vibrationally excited HCl($v = 1$ and 2) fragments was not reported for 193 nm photodissociation, a quantitative comparison of the vibrational distributions of HCl is not possible at this time. The REMPI spectra (Figure 2 of this work and Figure 1 in ref 9), however, demonstrate that the vibrational energy content of the HCl fragments from Scheme 1 is smaller than that of 193 nm photodissociation. Since the three-center HCl elimination has an exit channel barrier of 2.6 kcal/mol[18] which is much smaller than the vibrational spacings of HCl, from the vibrational point of view of HCl, the reaction path is almost like a simple bond fission which does not have a reverse barrier. Hence the vibrational distribution should be statistical and thus the colder vibrational distribution of HCl produced by Scheme 1 is as anticipated in terms of the total excitation energy difference between two excitation methods.

The branching ratio of two spin−orbit states of Cl is measured to be 0.15 ± 0.02, which is also colder than that of 193 nm photodissociation, 0.30 ± 0.05.[9,32] In the 193 nm photodissociation, Cl atoms are formed via two potential energy surfaces, the ground and excited (n,$\sigma^*$) potential energy surfaces. Huang et al. estimated that the branching ratios of Cl($^2P_{1/2}$) versus Cl($^2P_{3/2}$) are 0.16 for dissociation on the ground PES and 0.54 for dissociation on the excited PES, respectively.[11] The ground PES branching ratio of our excitation scheme is slightly lower than that of 193 nm photodissociation. If one consider the large difference of the excitation energies of two excitation methods, i.e., about 68 kcal/mol, this small difference of the branching ratio is rather surprising. In our excitation scheme, however, the average energy content of VC was estimated to be about 80 kcal/mol, which is almost 10 kcal/mol lower than the barrier to the C−Cl bond fission. It means that the average energy content of the VC molecules undergoing the C−Cl bond fission is much higher than that of all VC molecules even though those constitute only a small fraction of all VC molecules prepared. Hence the fact that the branching ratio of two spin−orbit states of the Cl atoms produced by Scheme 1 is slightly lower than the value of the 193 nm photodissociation is not unreasonable.

## 5. Conclusions

It is successfully demonstrated in this work that the secondary intramolecular H-atom migration may be used to excite various ethylenes in the ground electronic state. The amount of the released energy during the isomerization is large enough to initiate the unimolecular dissociation in the ethylenes excited via this scheme. Ketenes may also be used as the precursors for vibrationally hot ethylenes in addition the diazirines, one of which was employed in this work.

The HCl and Cl fragments were identified as in 193 nm photodissociation but the dissociation dynamics of VC excited via Scheme 1 were found to be quite different from those of 193 nm photodissociation. Since the average excitation energy was much lower than that of 193 nm photodissociation, the overall state distributions of the HCl and Cl fragments were much colder than those of 193 nm photodissociation. The smaller average excitation energy of VC prepared by Scheme 1 does not provide enough energy for vinylidene to isomerize during the fragmentation event. Hence the excess energy released in the subsequent isomerization of vinylidene does not contribute to the rotational energy distribution of HCl($v = 0$) which shows a Boltzmann behavior giving the rotational temperature of 470 K. It seems to us that the low-temperature component in the rotational distribution of the HCl($v = 0$) fragments observed in the 193 nm photodissociation originates from the excited PES leading to HCl($X^1\Sigma^+$) and $H_2C{=}C$:($^3B_2$).[37,38] The excitation energy of VC excited by Scheme 1 is not high enough to reach the excited PES and thus the low-temperature component was not observed in our work.

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