

Distribution of Rotational States in Half-Collisions: 193-nm Photolysis of Dichloroethylene Isomers

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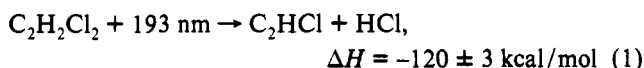
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The photodissociation of *cis*-, *trans*-, and 1,1-dichloroethylene (DCE) was studied by a pump-and-probe technique, using a 193-nm excimer laser to excite the parent molecule and time-of-flight resonance-enhanced multiphoton ionization to detect the products. We report here the nascent rotational state distributions of $\text{HCl}(v''=0,1,2)$ and also the relative yields and intensity dependencies of HCl , H , $\text{Cl}(^2\text{P}_{3/2})$, $\text{Cl}(^2\text{P}_{1/2})$, HCl^+ , and Cl^+ . Our finding that the rotational state distributions of HCl for all three isomers are very similar leads us to conclude that the nascent distribution is determined far along the reaction coordinate and is insensitive to the isomeric form of the parent molecule, regardless of whether photoelimination results from a three- or four-center transition state. We also observed qualitatively different behavior for $\text{HCl}(v''=0)$ and $\text{HCl}(v''=1,2)$. As in our previous study of vinyl chloride, we found that $\text{HCl}(v''>0)$ has a Boltzmann-like rotational state distribution, with temperatures in this case near 1400 K, whereas the distribution for $v''=0$ is described by a biexponential function with a low J'' temperature around 300 K and a high J'' temperature around 10 000 K. We propose that the dichotomy between these two distributions is due to microscopic rather than chemical branching. The relative yields of HCl and Cl^+ for *trans*-DCE are approximately double those of *cis*- and 1,1-DCE. This result is consistent with the interpretation that the yield-determining step is faster than *cis*-*trans* isomerization. The yields of all the other products are the same for *cis* and *trans*. For 1,1-DCE the yields of H , $\text{Cl}(^2\text{P}_{1/2})$, and HCl^+ are much greater than for *cis*- and *trans*-DCE, while for $\text{Cl}(^2\text{P}_{3/2})$ the 1,1-DCE yield is somewhat smaller. The relative yields of H and $\text{Cl}(^2\text{P}_{3/2})$ can be explained by the stabilities of the organic fragments, while the HCl^+ yields can be explained statistically. All of the neutral fragments were found to be produced by single-photon processes, while HCl^+ and Cl^+ require three and four photons, respectively. Ladder climbing mechanisms are proposed for the two ionic fragments.

Introduction

The close relationship between product state distributions in bimolecular collisions and photodissociation ("half-collisions") was pointed out by Dudley Herschbach nearly 20 years ago.¹ As he noted, elucidation of the mechanism for bimolecular reactions is frequently complicated by the average over impact parameters and orientation of the reactants. In contrast, photodissociation reactions are initiated at a turning point where the geometry of the parent molecule is well-defined. Much can be learned about the reaction dynamics by measuring the energy and angular momentum distributions of the fragments for different initial states of the parent molecule.

An interesting opportunity arises when different isomers of the parent molecule are available. An example is the ultraviolet photoelimination of HCl from 1,1-, *cis*-, and *trans*-dichloroethylene (DCE)²



where ΔH is the total available energy. If we think of the elimination of HCl as a simple, concerted process, then very different product rotational states of HCl are expected for the three isomers. For the 1,1 isomer HCl is eliminated by a four-center (α,β) mechanism involving both carbon atoms. For the *cis* isomer a three-center (α,α) mechanism applies, with the H and Cl atoms departing from the same carbon atom, while for the *trans* compound both mechanisms may contribute. The different transition states leading to α,α and α,β elimination should produce different torques acting on the departing fragments, which would be reflected in the rotational state distribution of the HCl product. In reality, the mechanism need not be concerted. The 193-nm photon absorbed by the parent molecule provides sufficient energy for rotation about the $\text{C}-\text{C}$ bond as well as for 1,2 migration

of the hydrogen atoms. These processes may compete with the elimination reaction and thereby alter the product state distribution.

The present study is part of an ongoing investigation of the photodissociation dynamics of halogenated ethylenes. In an earlier paper Reilly et al.³ reported the rotational state distributions for $\text{HCl}(v''=0,1,2)$ produced in the 193-nm photodissociation of vinyl chloride (VCl). In that study they found strikingly different distributions for $\text{HCl}(v''=0)$ and $\text{HCl}(v''>0)$. The former displayed a non-Boltzmann distribution with a low-energy part ($J'' \leq 6$) that could be described by a temperature of 340 K and a high-energy part ($7 \leq J'' \leq 13$) that is nearly flat with a "temperature" around 20 000 K. In contrast, the distributions for $v''=1$ and 2 could be fit to a Boltzmann function with temperatures around 2000 K. It was tempting to assign the first distribution to α,α and the second to α,β elimination. A primary motivation for the present study was to see whether the two types of distributions also occur for the dichloroethylene compounds, with perhaps the different isomers showing a preference for one or the other.

In a second study Mo et al.⁴ explored a number of other dissociation pathways for various chlorinated ethylene compounds. One of the processes they characterized is a two-photon elimination of electronically excited HCl . This reaction path was apparent from a three-photon HCl^+ signal which was observable with just the unfocused 193-nm laser. A further goal of the present study is to determine whether this process occurs also for the dichloro compounds and, if so, to discover how the reaction rate depends on isomeric structure of the molecule.

Although there are no published data on the rotational state distributions of HCl eliminated from DCE, there have been some studies of the vibrational and translational energy distributions of the fragments. Berry⁵ has used chemical laser techniques with flash lamp excitation of DCE to measure the relative populations

of $\text{HCl}(v''=0-3)$. He found the vibrational energy content of HCl to increase in the order $\text{trans} < \text{cis} < 1,1$. Donaldson and Leone⁶ used FTIR spectroscopy to measure the vibrational populations of $\text{HCl}(v''=1-4)$ produced from *trans*-DCE at 193 nm. The average vibrational energies obtained in the two studies are in good agreement, although the detailed distributions differ somewhat. Moss et al.⁷ observed infrared fluorescence from the organic fragments produced from all three isomers at 193 nm. Their data revealed considerable vibrational excitation of the fragments, with *cis*- and *trans*-DCE giving very similar spectra. Finally, Umemoto et al.⁸ measured the translational energy distributions of HCl from all three isomers. They found that the peak in the distribution is $\approx 6\%$ of the total available energy, while the maximum fraction of kinetic energy is $\approx 35\%$.

Experimental Section

Since the experimental apparatus was described in detail previously,⁹ we will present here only a brief summary. Our apparatus is a pulsed molecular beam machine equipped with a standard Wiley-McLaren¹⁰ time-of-flight (TOF) mass spectrometer. We performed two types of experiments with this apparatus. In the first set of experiments a pump-and-probe technique was used. An ArF (193 nm) excimer laser (Lambda Physik EMG150) was used to photodissociate the dichloroethylenes, while the product HCl was probed by $2 + 1$ resonance-enhanced multiphoton ionization (REMPI), using a frequency-doubled excimer-pumped dye laser (Lambda Physik EMG102/FL2002). In the second set of experiments a single excimer laser was used both to dissociate the parent molecules and to ionize the fragments. In both experiments the ion signal was detected with a dual microchannel plate and averaged with a boxcar. The TOF detector was equipped with deflection plates which enabled us to shutter out all ions other than HCl^+ and Cl^+ . The gated integrator could readily distinguish between the arrival times of these remaining ions.

In the pump-and-probe experiments the two laser beams were counterpropagated along an axis that was perpendicular to both the molecular beam and the TOF detector, passing through a point midway between the repeller and extractor electrodes. The DCE molecular beam was introduced into the reaction chamber with a pulsed valve (Newport BV-100V) fitted with a Teflon tip located approximately 3 cm from the optical axis.

The $\text{HCl}(v''=0,1,2)$ REMPI spectra were obtained using $\text{F}^1\Delta$ as an intermediate Rydberg state. For all three isomers we scanned the fundamental wavelength from 481 to 486 nm to obtain the $\text{HCl F-X}(0,0)$ and $(1,1)$ bands and from 498 to 503 nm for the $\text{HCl F-X}(0,1)$ and $(1,2)$ bands, using Coumarin 480 and 500 dyes. In addition, we also detected H , $\text{Cl}(^2\text{P}_{3/2})$, and $\text{Cl}(^2\text{P}_{1/2})$, setting the fundamental of the probe laser at 486.02, 475.34, and 475.48 nm.¹¹ In these experiments the pump laser fluence was typically 10 mJ/cm^2 , while the probe laser energy was typically $0.5\text{--}1.0 \text{ mJ/pulse}$. The latter was focused with a 15-cm lens to a spot size of $\sim 0.1 \text{ mm}$. Both laser intensities were monitored continuously in order to normalize the spectra.

For most of the spectra, dissociation of DCE by the probe laser was negligible, and an average of 10 laser shots per step was sufficient to obtain a satisfactory signal/noise ratio. When dissociation by the probe laser was observed (though always much less than from the pump laser), we measured the difference between the signals with the pump laser turned on and off in alternating shots of the dye laser. In this case a total of 30 shots were averaged per grating step.

The time interval between the pump and probe lasers was typically 500 ns. This delay was chosen to discriminate against HCl^+ produced by the pump laser alone. In order to test for the possibility that collisions in the beam may have relaxed the rotational population of the nascent HCl , we recorded a number of spectra with delay times of 300, 500, 1000, and 2000 ns. No evidence of rotational relaxation was found.

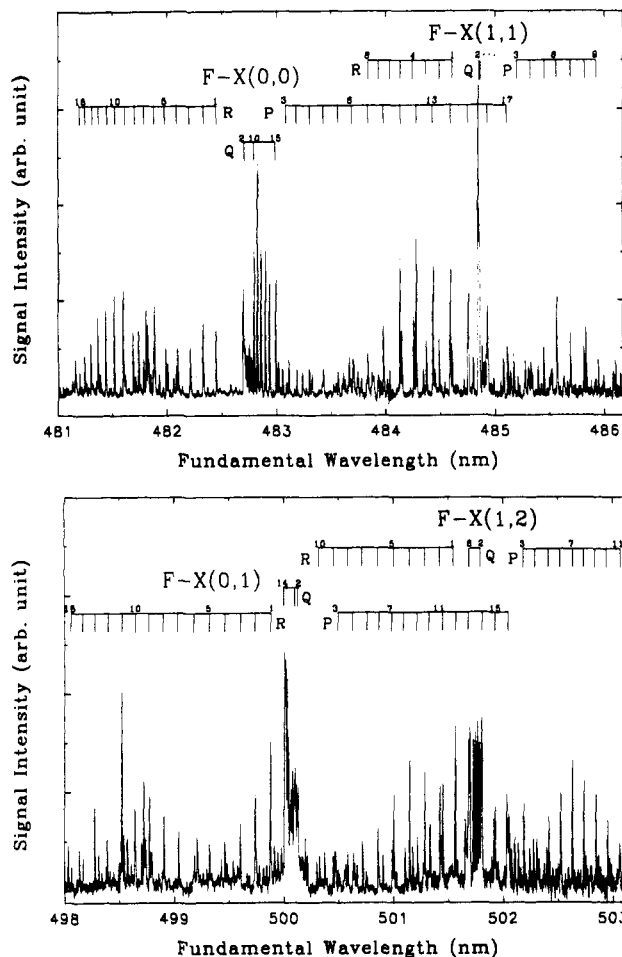


Figure 1. Multiphoton ionization spectrum of HCl produced from *trans*-DCE.

In the second set of experiments we used a focused ($f = 38 \text{ cm}$) 193-nm laser to photodissociate DCE, producing HCl^+ and Cl^+ ions. The laser power, HCl^+ signal, and Cl^+ signal were recorded for each laser shot. The laser power was varied continuously by passing the beam through an absorption cell containing a variable amount of ammonia gas.⁴ The ion signals and laser intensity were recorded on every shot, giving 1–2 orders of magnitude variation in laser intensity for a single run.

The purity of the DCE samples was checked by NMR spectroscopy, which confirmed the manufacturer's (Aldrich) claimed purities (*trans*-DCE, 99%; *cis*-DCE, 97%; 1,1-DCE, 98%). The reagents were used without further purification. The neat DCE vapor was stored in a reservoir and admitted into the nozzle with a stagnation pressure of $\sim 200 \text{ Torr}$.

Results

The experimental results consist of (i) the rotational state distributions of HCl for vibrational levels $v'' = 0, 1$, and 2 , (ii) the relative quantum yields of HCl , H , $\text{Cl}(^2\text{P}_{3/2})$, $\text{Cl}(^2\text{P}_{1/2})$, HCl^+ , and Cl^+ , and (iii) the intensity dependence of the products. These quantities were measured for all three DCE isomers.

The rotational state distributions were determined from the $2 + 1$ REMPI spectrum of the $\text{F-X}(v',v'')$ transitions. The spectrum for *trans*-DCE is shown in Figure 1. The vibrational bands that were assigned and calibrated are $(0,0)$, $(1,1)$, $(0,1)$, and $(1,2)$. Whenever possible, P, Q, and R branches were used. In Figure 2 the Q branch for the $(0,0)$ transition is shown for each of the isomers.

The rotational state populations may be extracted from the spectrum using the well-known expression¹²

$$I(v',J';v'',J'') = CP(v'',J'') q(v',v'') S(J',J'')/(2J'' + 1) \quad (2)$$

where $I(v',J';v'',J'')$ is the signal intensity corresponding to the

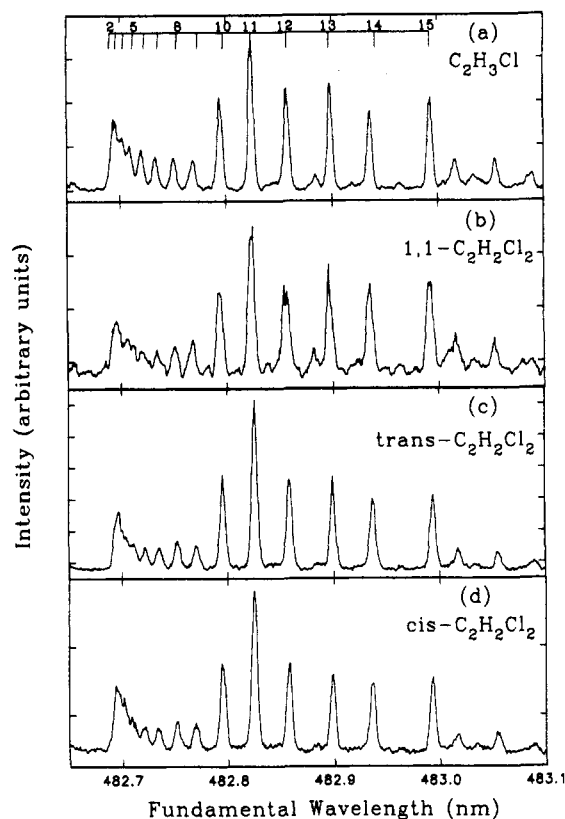


Figure 2. Q branch of the $F \leftarrow X(0,0)$ transition of HCl produced from vinyl chloride and the three DCE isomers.

$F(v',J') \leftarrow X(v'',J'')$ transition, C is an apparatus constant, $P(v'',J'')$ is the population of the ground state, $q(v',v'')$ is the Franck-Condon factor, and $S(J',J'')$ is the rotational line strength. From the observed signals (peak heights) we can determine the relative rotational state distribution within a single vibrational band, provided that the line strength factor is known. If the upper state were unperturbed, this quantity would simply be the Hönl-London factor. But in fact the F state is strongly perturbed.⁹ This is especially evident in the Q branch of the (0,0) transition (see Figure 2), which has a peculiar bimodal appearance. This intensity anomaly is due in part to a predissociative process which depletes the population for $J' = 3-9$. The effective rotational line strengths have been determined experimentally from a room temperature sample of HCl.⁹ Care was taken to ensure that the experimental conditions for obtaining the correction factors were as close as possible to those used in measuring the rotational populations of HCl produced from DCE. The resulting population distributions for $v'' = 0, 1$, and 2 are shown in Figures 3-5 in the form of "Boltzmann plots".

In a second set of experiments we measured the relative yields of the atomic, molecular, and ionic products. These yields were measured relative to those of the 1,1 isomer for which they are defined as unity. The results are listed in Table I. The relative quantum yields for different fragments from the same parent molecule have been presented in the earlier paper by Mo et al.⁴ In the present study we remeasured the branching ratio of $\text{Cl}(^2P_{1/2})$ to $\text{Cl}(^2P_{3/2})$ for *trans*-DCE. The signal ratio was 0.074 ± 0.007 , in excellent agreement with the earlier value of 0.06 ± 0.01 . Applying the recently reported calibration factor of Tonukura et al.,¹³ we obtain a product ratio of 0.19.

In order to compare the product yields for different isomers, we measured the absorption coefficients at 193 nm. The results, which are listed in Table II, are in good agreement with the synchrotron measurements of Berry.⁵ The relative yields listed in Table I for all the fragments except HCl^+ and Cl^+ (which require absorption of more than one photon) have been corrected for the different absorption cross sections.

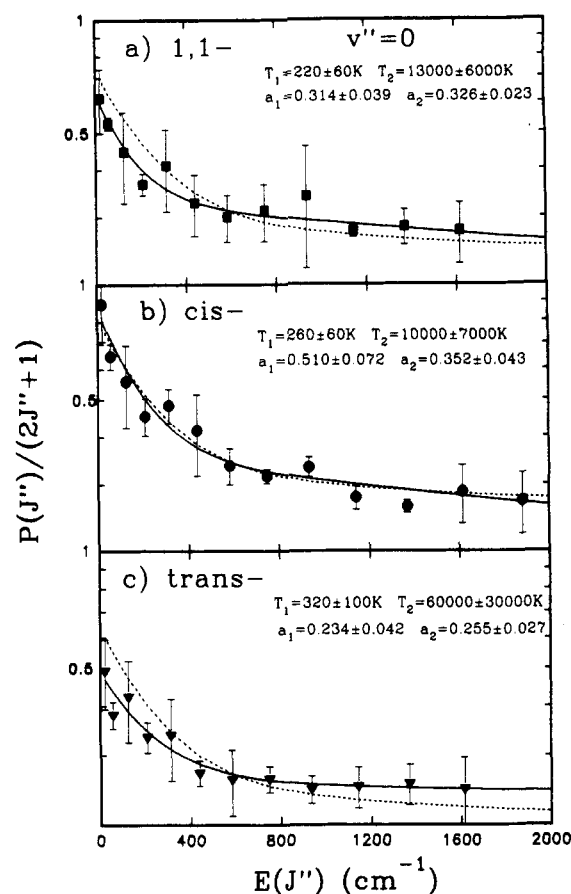


Figure 3. Boltzmann plots of the nascent rotational populations of HCl ($v''=0$) produced by photodissociating 1,1-, *cis*-, and *trans*-DCE. The populations were calculated from the peak heights in the REMPI spectrum using empirical line strength factors. The solid curves are least-squares fits of the a biexponential function (eq 3), with fitted values of the parameters listed in each panel. The dashed curves are the least-squares fit of the vinyl chloride data reported in ref 3.

In a third set of experiments we measured the laser intensity dependence of the various products. We always found that at low laser intensity I_L the signal obeys a power law I_L^n , where n is a constant, while at higher intensity n falls off, indicating the onset of saturation. The fitted values of n are listed in Table III. We previously established for vinyl chloride⁴ that HCl elimination is a single-photon process, and in trial runs we confirmed that this is the case for DCE as well. More detailed studies of the intensity dependence of the H , $\text{Cl}(^2P_{3/2})$, and $\text{Cl}(^2P_{1/2})$ yields established that these fragments are also produced with a single photon. In contrast, the HCl^+ and Cl^+ fragments require three and four photons, respectively. This is seen in Figure 6 where n is greater than 2 for HCl^+ and greater than 3 for Cl^+ . While the uncertainty of the absolute intensity calibration may be as large as 50%, the relative intensity scales for the three isomers are accurate.

Discussion

A. Rotational State Distributions. The HCl rotational distributions have a number of striking properties. First, the distributions for $v'' = 0$ and $v'' > 0$ are qualitatively different. For $v'' > 0$ the data can be described empirically by a Boltzmann distribution characterized by a "temperature" T , while for $v'' = 0$ a biexponential formula

$$P(J'')/(2J''+1) = a_1 \exp(-E(J'')/kT_1) + a_2 \exp(-E(J'')/kT_2) \quad (3)$$

is required. This dichotomy was observed previously for vinyl chloride.³ Second, the distributions are nearly the same for all three isomers. They are also similar to those found previously

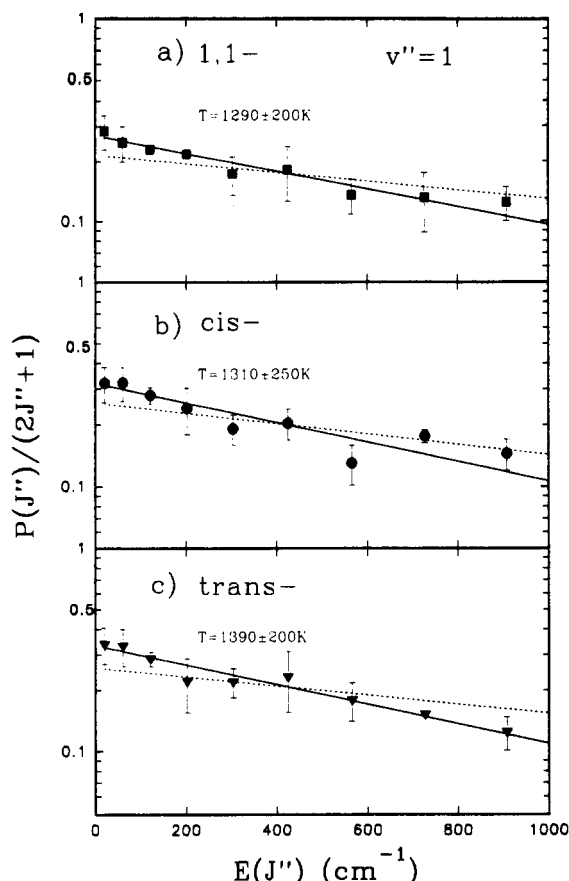


Figure 4. Same as Figure 3, only for $\text{HCl}(v''=1)$. The solid line is a least-squares fit of a Boltzmann distribution, with the fitted temperatures listed in each panel. The dashed lines are the phase space model calculation described in the text.

for VCl , for which the available energy is only slightly greater (124 vs 120 kcal/mol).

A closer look shows some subtle differences both between DCE and VCl and also among the different DCE isomers. For $v'' > 0$ the fitted temperature for VCl is around 2000 K, while for all three DCE isomers it is near 1400 K. The temperatures for $v'' = 0$ are more difficult to establish since the data are of insufficient quality to fit four independent parameters accurately. All that we can say is that for VCl and all three isomers of DCE T_1 is approximately 300 K and T_2 is on the order of 10 000 K. The ratio of preexponential factors a_1/a_2 , on the other hand, could be determined with an accuracy of about 20%, as is evident from just a visual inspection of the curvature in the Boltzmann plots (Figure 3). For VCl and *cis*- DCE $a_1/a_2 = 1.5 \pm 0.3$, while for *trans*- and 1,1- DCE the ratio is 0.9 ± 0.2 . Both effects—the variation in Boltzmann temperature for $v'' > 0$ and in a_1/a_2 for $v'' = 0$ —are significant at the confidence level of a single standard deviation. Finally, the vibrational distribution for *trans*- DCE appears to be slightly colder than for the other two isomers, as seen in Table I. While these differences between the state distributions for the three DCE isomers and VCl appear to be real, it is the overall similarity of the distributions that is most striking and which suggests a common mechanism.

Several experiments were performed to rule out possible artifacts. Since the $F(v=0)$ state of HCl has a J -dependent perturbation,⁹ we were concerned that the differences between the rotational state distributions for $v'' = 0$ and $v'' > 0$ might possibly be due to errors in the empirical line strength correction factors. We ruled out this possibility by three independent tests. First, for low values of $J''(v''=0)$ we used also the $E^1\Sigma^+(v''=0) \leftarrow X^1\Sigma^+(v''=0)$ transition, confirming that the curvature in the Boltzmann plot is real. Second, for $v'' = 1$ we used both the $F(1,1)$ and the $F(0,1)$ transitions. The results were identical

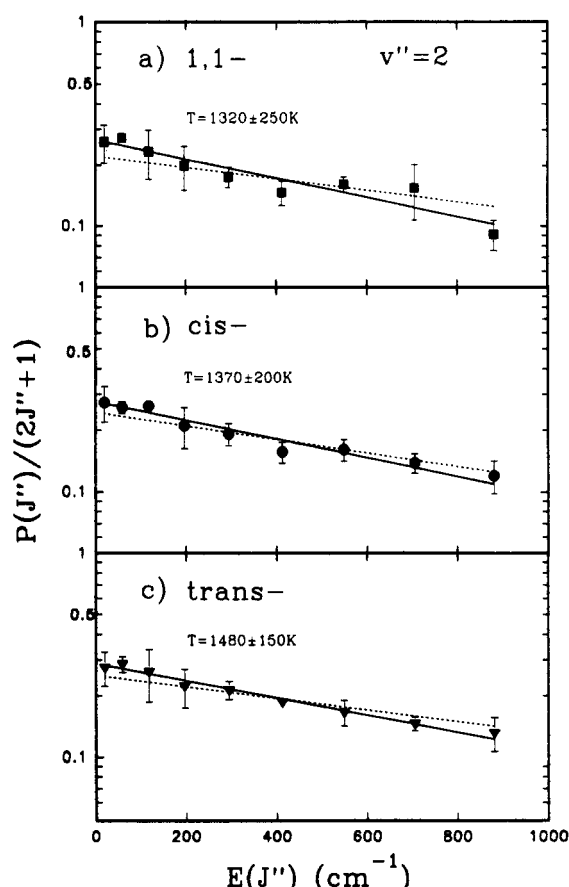


Figure 5. Same as Figure 4, only for $\text{HCl}(v''=2)$.

TABLE I: Relative Product Yields^a

fragment	relative yield	
	cis	trans
$\text{HCl}(v=0)$	1.3 ± 0.3^b	2.2 ± 0.3
$\text{HCl}(v=1)$	1.1 ± 0.2	1.8 ± 0.2
$\text{HCl}(v=2)$	1.2 ± 0.3	1.6 ± 0.3
H	0.26 ± 0.05	0.33 ± 0.04
$\text{Cl}(^2P_{3/2})$	1.3 ± 0.1	1.3 ± 0.2
$\text{Cl}(^2P_{1/2})$	0.57 ± 0.06	0.49 ± 0.06
HCl^+	0.22 ± 0.02	0.25 ± 0.03
Cl^+	1.0 ± 0.1	$1.6 \sim 2.0$

^a Yield for the 1,1 isomer is set to unity. ^b Uncertainties for the relative quantum yields are a single standard deviation for repeated runs. For $\text{HCl}(v)$ the quantum yields for each rotational branch were included individually in the average.

TABLE II: Absorption Cross Sections of DCE at 193 nm

isomer	cross section (10^{-18} cm^2)
1,1	32.9 ± 2.8
cis	31.0 ± 2.5
trans	37.9 ± 2.5

within experimental scatter, even though perturbations of the upper states are very different. Third, in a companion study¹⁴ we photolyzed partially deuterated VCl (CH_2CDCl). The DCl and HCl Boltzmann plots were identical to the HCl distribution obtained with normal VCl , even though the perturbation in DCl occurs in a different part of the spectrum. In another study, variation of the time delay between the pump and probe lasers by an order of magnitude ruled out the possibility that the low J populations for $v'' = 0$ may be contaminated by rotational relaxation.

We consider next the possible origins of the dichotomy between the $v'' = 0$ and $v'' > 0$ distributions. A plausible explanation is that one distribution comes mainly from α, α elimination of HCl and the other from α, β elimination. For this to be possible the

TABLE III: Intensity Dependence of Photofragments^a

fragment	<i>n</i>		
	1,1	cis	trans
H	0.97 ± 0.04	0.97 ± 0.04	0.95 ± 0.05
Cl(² P _{3/2})	0.94 ± 0.06	0.99 ± 0.04	0.96 ± 0.04
Cl(² P _{1/2})	0.99 ± 0.03	1.00 ± 0.03	0.98 ± 0.03
HCl ⁺	2.6 ± 0.1	2.8 ± 0.1	2.7 ± 0.1
Cl ⁺	3.4 ± 0.2	3.3 ± 0.2	3.8 ± 0.2

^a Uncertainties for *n* are either the standard deviations obtained from the least-squares fits of the intensity plots or the standard deviations in fitted values of *n* from multiple runs, whichever is larger.

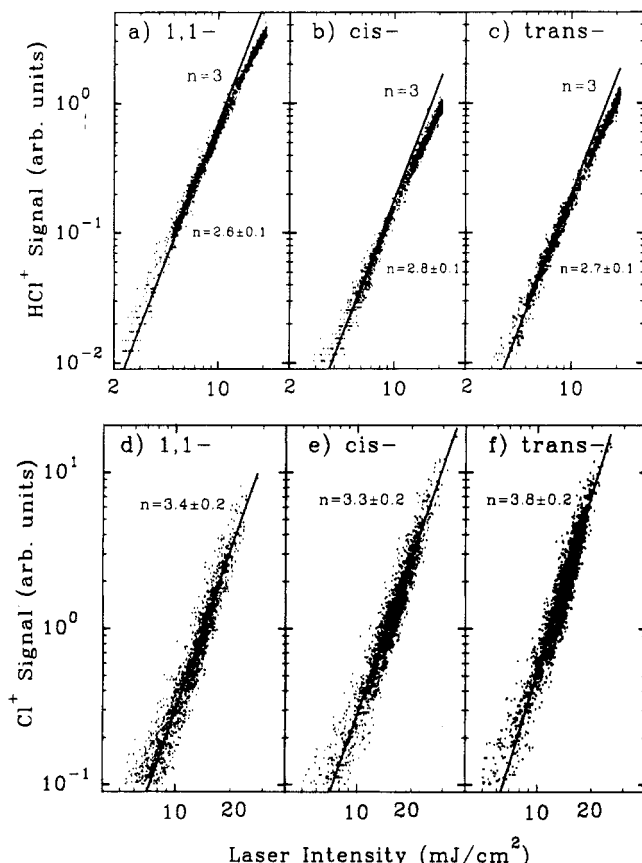


Figure 6. Intensity dependence of HCl⁺ (upper panel) and Cl⁺ (lower panel) signals measured with a focused ArF laser. The solid lines in all six plots are least-squares fits of a power law, with the fitted value of the exponent listed in each plot. Also shown for reference in the HCl⁺ plots is a cubic power law.

transition states for the two processes should have comparable barrier heights. For vinyl fluoride, Kato and Morokuma¹⁵ indeed calculated that the barriers for α,α and α,β elimination have nearly the same energies. One might imagine that a similar situation exists for DCE, with each process yielding a unique product state distribution. Nevertheless, our observation that the distributions are insensitive to isomeric changes argues against this explanation. More conclusive evidence comes from our study of VCl-d₁.¹⁴ This study showed definitively that the product rotational distributions are identical for three- and four-center elimination.

We are forced to conclude that the rotational state distribution of HCl depends only weakly on the geometry of the transition state and is determined much later along the reaction coordinate. At first glance this is a startling result since the carbene that is produced in the α,α process has some 40 kcal/mol more internal energy than the acetylene fragment produced by α,β elimination. The insensitivity of the HCl state distribution to the electronic energy of the organic fragment can be understood if we compare the time scales for HCl recoil and vinylidene-acetylene isomerization. Lineberger¹⁶ and co-workers have determined that the

lifetime of vinylidene is between 40 and 200 fs. In the present case, where the fragments contain a considerable amount of internal energy, the lifetime is likely to be even shorter. In contrast, if HCl elimination occurs on the ground potential energy surface, dissociation should occur on a picosecond time scale. On this scale the acetylene and vinylidene fragments would appear to be a single, highly energetic species which fluctuates rapidly between two isomeric states. The observed rotational state distribution of HCl would be determined by torques which have no memory of the original transition state.

Nevertheless, the different rotational distributions for $v'' = 0$ and $v'' > 0$ strongly suggest a dual mechanism. Since we have eliminated the competition between α,α and α,β elimination (what we might call "chemical branching") as a possible explanation, we must look for dynamical alternatives ("microscopic branching") within the same chemical pathway. Microscopic branching is well-known in bimolecular reactions,¹⁷ and there is no reason why it should not occur as well for "half-collisions".

We consider first the case of $v'' > 0$. The observation of a Boltzmann rotational state distribution suggests a statistical process. To examine this possibility further, we performed a simple phase space calculation in which only the total energy is conserved. Letting $J'', v'', J_C, E_{\text{int}}$, and E_t represent the rotational and vibrational quantum numbers of HCl, the rotational quantum number and internal energy of the organic fragment, and the relative kinetic energy of the products, respectively, the prior distribution¹⁸ is given by

$$P(J'', v'', J_C, E_{\text{int}}) = C(2J'' + 1)\rho(E_{\text{int}})E_t^{1/2} \quad (4)$$

where *C* is a normalization constant and ρ is the vibrational density of states of the organic fragment. The prior distribution of J'' and v'' is obtained by summing over J_C and integrating over E_{int} , using the Whitten-Rabinovich¹⁹ density of states and conserving energy.

For a total available energy of 120 kcal/mol, the model predicts a Boltzmann-like rotational state distribution with a temperature of 7900 K for $v'' = 1$ and 7400 K for $v'' = 2$ for all three isomers. For VCl the model predicts temperatures that are 8% higher. The experimental temperatures are considerably lower, with a ratio (VCl vs DCE) of 1.6 ± 0.3 for $v'' = 1$ and 1.3 ± 0.2 for $v'' = 2$. Better agreement is obtained with this simple model if not all of the exoergicity is available to HCl. The reverse reaction of HCl + HCCH has a barrier of approximately 45 kcal/mol, estimated from the thermal activation energy for photodissociation of VCl.²⁰ If we think of this barrier as the energy needed to reorganize the H-Cl, C-Cl, and C-H bonds to form the transition state, then this value provides a rough estimate of the localized energy that is available to HCl in the forward direction. In addition, some fraction of energy above the barrier might also be available.²¹ An empirical value for the localized energy proposed by Umemoto et al.⁸ is the maximum relative kinetic energy of the separating fragments, which they found to be 40 ± 5 , 45 ± 5 , and 45 ± 5 kcal/mol for *cis*-, *trans*-, and 1,1-DCE, respectively. Adopting these values for the localized available energy, the phase space model predicts a Boltzmann distribution of rotational states with temperatures of 2400 K ($v'' = 1$) and 1900 K ($v'' = 2$) for *cis*-DCE and 2700 K ($v'' = 1$) and 2200 K ($v'' = 2$) for both *trans*- and 1,1-DCE. While these temperatures are still hotter than the observed ones, they are in qualitative agreement with the data. More importantly, the ratios of the predicted temperatures for VCl vs DCE are 1.5–1.6 for $v'' = 1$ and 1.3–1.5 for $v'' = 2$, which are in excellent agreement with experiment.

The phase space model greatly underestimates the vibrational energy of HCl, even when the full 120 kcal/mol is available. This is consistent with the finding of previous investigators^{5,6} that in order to fit the vibrational populations with a statistical model it was necessary to assume a lower vibrational frequency for HCl.

The picture which emerges is that the vibrational population is determined much earlier along the reaction coordinate. At this stage of the reaction, the isomer of the parent molecule can affect the partitioning of internal energy of the fragments. Each vibrational state of HCl then evolves independently, with freezing of the rotational state distribution occurring only much later along the reaction path.

The biexponential rotational state distribution for $v'' = 0$ suggests the existence of a second mechanism. One possibility for microscopic branching is the competition between concerted and stepwise elimination of HCl. We might imagine the non-Boltzmann distribution for $v'' = 0$ coming from a concerted elimination (either three-center or four-center), while the quasi-statistical distribution for $v'' > 0$ arises from some sequential process.

It is instructive to compare HCl elimination from VCl with H_2 elimination from ethylene. In the latter case, Pople and co-workers²² predicted that the lowest energy path is α, α elimination, with a barrier height of 74.2 kcal/mol. The second lowest energy path is a 1,2 hydrogen atom shift followed by three-center elimination of H_2 , with a barrier height of 93.4 kcal/mol. The ethylidene intermediate was found to be an unstable structure along this energy path. A direct four-center elimination was ruled out since its barrier height is 109.3 kcal/mol. In contrast, for vinyl fluoride Kato and Morokuma²³ found that direct α, α and α, β elimination of HF have barriers of 79.8 and 81.0 kcal/mol, while a 1,2 shift occurs at the much higher energy of 111.5 kcal/mol. Morokuma et al.²⁴ also found for formaldehyde that when the α hydrogen is replaced by a fluorine atom the barrier for a 1,2 H atom shift is 25 kcal/mol higher than for direct elimination of HF. Similarly, for DCE we expect that a 1,2 shift of the H atom has a much higher barrier than direct HCl elimination. We accordingly rule out the migration of a hydrogen atom from one carbon to the other as the first part of a stepwise mechanism.

Without detailed knowledge about the potential energy surfaces, we can only speculate about the nature of the nonconcerted process. Further theoretical and experimental work is clearly needed. In particular, measurements of the relative kinetic energy distributions as a function of v'' and J'' would help to distinguish between concerted and stepwise mechanisms.²⁵

B. Product Yields. In Table I we show that the relative yields of HCl for the 1,1, cis, and trans isomers are in the approximate ratio of 1:1:2. The greater yield for *trans*-DCE might be a simple consequence of the availability of both α, α and α, β pathways for this isomer, as compared with only α, β elimination for 1,1-DCE and α, α elimination for *cis*-DCE. This argument works, however, only if elimination is rapid compared with rotation about the C–C bond. The barrier to *cis*–*trans* isomerization of DCE is only 57.4 kcal/mol,²⁶ as compared with a total available energy of 120 kcal/mol. On the photoexcited π, π^* surface, one CH_2 or $CHCl$ group is twisted 90° with respect to the other.²⁷ On both potential energy surfaces, therefore, rotation about the C–C bond should be facile.

Another possible explanation is that different electronic states of the isomers are simultaneously excited. For the *trans* compound 193 nm lies on the short wavelength side of the absorption maximum, while for 1,1 it lies near the peak and for *cis* it lies on the long wavelength side.⁵ This explanation can be tested by measuring the relative yields as a function of wavelength. We feel that this is an unlikely explanation since for all three isomers the very large oscillator strength (around 0.4 at the maximum) is carried by the same $\pi \rightarrow \pi^*$ transition.

A third possibility is that the relative yields reflect different internal conversion rates of the isomers. Our hypothesis is that very rapid internal conversion to the ground electronic surface is followed by slow elimination (concerted or otherwise) on the

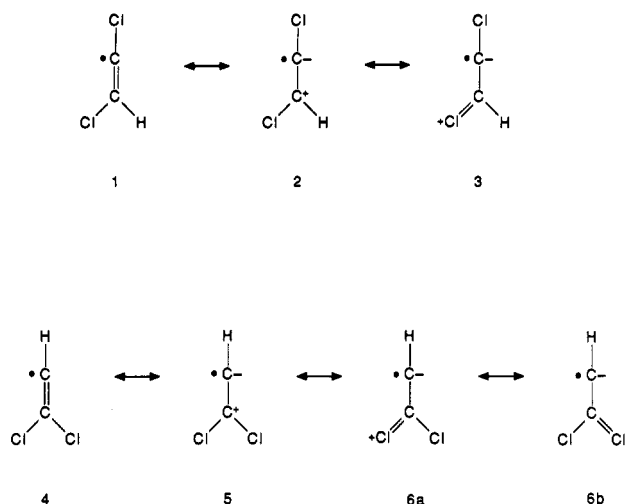


Figure 7. Resonance structures of the organic fragments produced by elimination of Cl atoms from 1,1- and 1,2-DCE.

lower surface.⁴ The matrix elements for surface crossing are likely to vary for the three isomers, resulting in different HCl yields.

A very different situation occurs for HCl^+ . As is discussed in the following section, we previously established that this product is the result of two-photon elimination of electronically excited HCl followed by one-photon ionization.⁴ As shown in Table I, the yields in this case are 4:1:1 for 1,1, *cis*, and *trans*. The equal yields for *cis* and *trans* are plausible since we expect that two-photon absorption is slow compared with rotation about the C–C bond on an electronically excited surface. The greater yield for the 1,1 isomer can be understood in light of our recent study of $VCl-d_1$, which showed that HCl^+ is produced mainly by an α, β mechanism.¹⁴ Assuming that the excited state is twisted, we expect that for 1,1-DCE each Cl atom can react with either of two H atoms, while for *cis*- and *trans*-DCE there is only one H atom available on the opposite carbon.

For all of the atomic fragments (H , $Cl(^2P_{3/2})$, and $Cl(^2P_{1/2})$) the *cis* and *trans* yields are equal. This would be the result if dissociation were slow compared with rotation about the C–C bond. Previously,⁴ we showed that H atoms recoil isotropically, indicating that dissociation is indeed slower than rotation of the molecule. On the other hand, a substantial fraction of the Cl atoms recoil anisotropically. If we suppose that the internal conversion rates in this case are the same for *cis* and *trans*, then the identical atomic yields for these two isomers may simply reflect the fact that the local environments of the Cl and H atoms are very similar. For both *cis*- and *trans*-DCE the H atoms share their C atom with a Cl atom, while for 1,1-DCE the H atoms are attached to the same carbon.

Since 1,1-DCE is topologically distinct, it is not surprising that its product yields are also different. It is intriguing to speculate why in some cases the yield for 1,1 is greater than for *cis* and *trans* (i.e., the 1,2 isomers), while in others it is smaller. For H atoms the 1,1 yield is 3–4 times greater. For 1,2-DCE the electron-withdrawing nature of Cl atoms weakens the C–H bond. This is likely to be a small effect which would result in a larger yield for 1,2-DCE, contrary to what we observe. The correct explanation of the relative yields is more likely to lie with the relative stabilities of the organic fragments (structures 1 and 4 in Figure 7). Both radicals may have contributions from a zwitterionic structure^{28,29} having a positive charge on the β carbon atom (2 and 5). These zwitterions are stabilized by relocating the positive charge onto the Cl atom (3 and 6). The key point is that the zwitterion produced from the 1,1 radical is doubly stabilized by the availability of two resonance structures (6a and 6b), accounting for the larger H atom yield for this isomer.

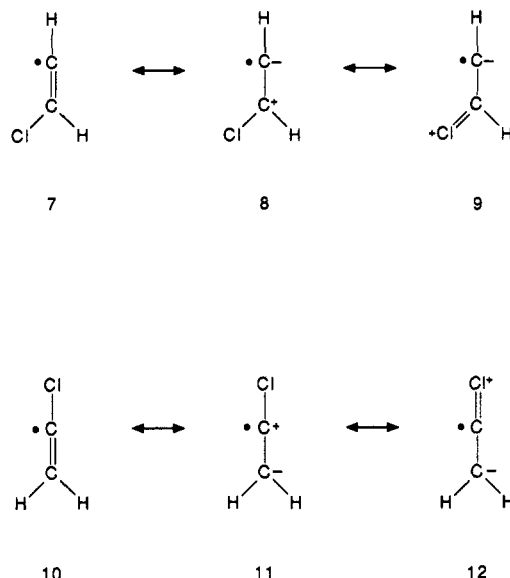


Figure 8. Resonance structures of the organic fragments produced by elimination of H atoms from 1,1- and 1,2-DCE.

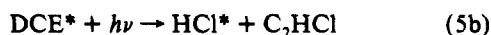
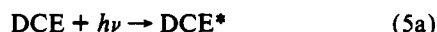
For $\text{Cl}(^2\text{P}_{3/2})$ atoms we observe the opposite trend, with the yield from 1,1-DCE being approximately 75% that of 1,2-DCE. In this case both zwitterions (structures 8 and 11 in Figure 8) are stabilized by only a single Cl atom. Here, however, the ionic structure produced from the 1,1 radical (10) is likely to be less stable because the unpaired electron resides on the positively charged carbon (11), leaving it with seven electrons in the resonant configuration (12). In the ion produced from the 1,2 radical (7) the unpaired electron lies on the negatively charged ion (8), and in the resonance structure (9) the stabilized carbon has a full octet.

Another interesting question is the branching fraction of $\text{Cl}(^2\text{P}_{1/2})$. While for ground-state atoms the yield from 1,1-DCE is approximately 75% that from 1,2-DCE, for $\text{Cl}(^2\text{P}_{1/2})$ it is approximately double. We know from past experience that the populations of the fine structure states are influenced by long-range forces.³⁰ We conclude that the asymptotic forces are sufficiently different for CH_2CCl and CHClCH to have a large effect on the fine structure (i.e., electronic) state of the Cl atom. This is in contrast with the asymptotic forces in the molecular elimination channel, where isomeric differences have very little effect on rotational (i.e., nuclear) motion.

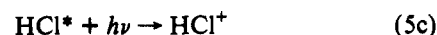
Finally, in the case of Cl^+ the relative product yields depend somewhat on laser intensity. Qualitatively, the Cl^+ yields resemble those of HCl, suggesting a common mechanism. This is discussed further in the following section.

C. Intensity Dependence of the Products. As in our study of VCl, we found that HCl, H, and Cl are all single-photon products. The only slightly surprising result is the H atom quantum yield. For ethylene Stowlow et al.³¹ found evidence of a two-photon mechanism, namely, slow photodissociation of ethylene followed by rapid photodissociation of the vinyl radical. For VCl and DCE, however, since the $\pi \rightarrow \pi^*$ transition is shifted to longer wavelengths, detachment of the first H atom is the dominant process at 193 nm.

While HCl^+ and Cl^+ are only minor products under our experimental conditions, they are interesting because of the window they provide for viewing what happens on higher potential energy surfaces. Previously, we showed that HCl^+ is the product of a $1 + 1 + 1$ resonant mechanism. Rewriting this for DCE, the mechanism is



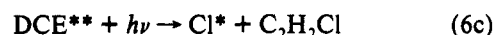
and



Summarizing our earlier findings,⁴ the principal evidence for a three-photon resonant process is the observation of a cubic intensity dependence at a fluence as low as 2 mJ/cm^2 .

Although we previously observed Cl^+ in VCl photolysis, this is the first report of this reaction channel. Our observation of $n > 3$ indicates that at least four photons are involved. One possible mechanism is reactions 5a–5c to produce HCl^+ , followed by photodissociation of the ion. We can rule out this mechanism because of the very different relative yields of HCl^+ and Cl^+ for different isomers listed in Table I.

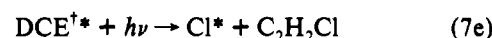
Another possibility is further “ladder climbing” in the DCE manifold followed by photodissociation to produce Cl^+ :



and



While this mechanism is not inconsistent with the data, it does not explain the similar relative yields for Cl^+ and HCl. Since the latter is believed to result from internal conversion to the ground state of DCE, a comprehensive mechanism for both products might be



and



In this mechanism DCE^\dagger refers to vibrationally excited DCE on the ground electronic surface. The step which links the yields of HCl and Cl^+ is (7b).

Conclusions

Most detailed studies of photodissociation dynamics have dealt with small molecules containing five or fewer atoms and only one chromophore. It is fascinating how the existence of two chromophores—in this case the carbon–carbon double bond and the chlorine lone pairs—can complicate the photodissociation dynamics, even for a molecule containing “only” six atoms. In this and our two preceding papers on the UV photodissociation of chloroethylenes, we have found abundant evidence for multiple reaction paths on both the ground and excited potential energy surfaces.

The main findings of the present study are summarized as follows:

1. The rotational state distributions of HCl produced from all three isomers of dichloroethylene are strikingly similar. All three have a biexponential distribution for $v'' = 0$ and a Boltzmann distribution for $v'' = 1$ and 2. These distributions are also very similar to those previously found for vinyl chloride. Since our recent work on partially deuterated VCl has shown that the state

distributions are the same for three-center and four-center elimination, we attribute the differences between $v'' = 0$ and $v'' > 0$ to "microscopic" rather than "chemical" branching.

2. Close examination reveals some slight variations in the product distributions. For *trans*- and 1,1-DCE, the preexponential coefficients a_1 and a_2 for $v'' = 0$ are approximately equal, while for *cis*-DCE and VCl they have a ratio of 1.5. For all three isomers the Boltzmann temperatures for $v'' > 0$ are approximately 1400 K, as compared with 2000 K for VCl. In addition, the vibrational state distribution for *trans*-DCE is slightly colder than for the other two isomers.

3. We have measured the relative yields of HCl, H, Cl($^2P_{1/2}$), Cl($^2P_{3/2}$), HCl $^+$, and Cl $^+$ for 1,1-, *cis*-, and *trans*-DCE. For HCl and Cl $^+$ the yield for *trans*-DCE is approximately double that of both the 1,1 and *cis* isomers. For the atomic fragments and HCl $^+$ the yields for *cis* and *trans* are identical, with the 1,1 yield being smaller for Cl($^2P_{3/2}$) and greater for the other products. The relative yields of Cl and H can be explained by the stabilities of the organic fragments.

4. The yields of the neutral products were all found to vary linearly with laser intensity, indicating that they were produced by a single photon. In contrast, HCl $^+$ requires three photons and Cl $^+$ at least four photons, both resulting from ladder climbing mechanisms.

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