Investigating the C−Cl Antibonding Character in the $\pi\pi^*$ Excited State of Vinyl, Allyl, and Propargyl Chloride: Emission Spectra and *ab Initio* Calculations

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Received: October 20, 1995; In Final Form: January 4, 1996⊗

We report the emission spectra of dissociating vinyl, allyl, and propargyl chloride upon photoexcitation at 199 nm. To provide a better understanding of the mixed electronic character in the Franck−Condon region of the excited states accessed, we also present *ab initio* calculations at the configuration interaction level for these three molecules. These experimental and theoretical results indicate large differences in the contribution of $n\sigma^*_{C-Cl}$ and $\pi\sigma^*_{C-Cl}$ character to these predominantly $\pi\pi^*_{C=C/C\equiv C}$ transitions. We present arguments based on the symmetry of the pertinent molecular orbitals to explain this observed variation. We conclude by considering how the differing electronic character of the excited state in these molecules may influence the branching ratios to C−Cl fission and HCl elimination products observed in the photodissociation of vinyl, allyl, and propargyl chloride.

Introduction

Unsaturated hydrocarbons with halogen substituents have been popular systems in photodissociation dynamics studies due to their accessible excited electronic states and the ease of detecting their photoproducts. In particular, vinyl chloride ($H_2C{=}CHCl$) has been extensively studied through a variety of experimental techniques which probe its photodissociation products.[1−5] Photodissociation of vinyl chloride in its first ultraviolet absorption band gives four different bond fission channels, two involving C−Cl fission and two involving HCl elimination. Recent crossed laser−molecular beam studies have also focused on the related systems allyl chloride[6,7] ($H_2C{=}CH{-}CH_2Cl$) and propargyl chloride[8,9] ($HC{\equiv}C{-}CH_2Cl$). These molecules show similar complexity in that they each dissociate through both C−Cl bond fission and HCl elimination channels. This study seeks to investigate the nature of the excited state accessed in these photodissociation experiments to better understand the observed photofragment dynamics.

In the photodissociation of vinyl chloride in its first ultraviolet absorption band, the branching between C−Cl fission and HCl elimination products has been investigated by a number of groups,[1,4,5] and there is good agreement on a C−Cl/HCl ratio of approximately 1:1. The observed C−Cl bond fission evidences two distinct kinetic energy distributions, both of which are peaked well away from zero kinetic energy, indicating significant exit channel barriers to reverse reaction for each of the two different C−Cl bond fission channels. Gordon and co-workers did a careful study of the HCl elimination channel,[3] and they find that HCl elimination occurs through 3- and 4-center processes. The exit channel barrier is believed to be particularly large for the 4-center process. The similarity of these HCl elimination reaction product distributions with the results of infrared multiphoton dissociation studies suggests that HCl elimination occurs following internal conversion to the ground state. Umemoto and co-workers speculate that, upon photoexcitation, twisting of the C=C bond leads to mixing of the $\pi\pi^*$ and $\pi\sigma^*$ configurations.[1] Internal conversion to the $\pi\sigma^*$ state may serve as an intermediate state which facilitates eventual internal conversion to the ground state.

Recent crossed laser−molecular beam studies in our laboratory have investigated the photodissociation of allyl chloride in its first ultraviolet absorption band.[6] These studies find only one C−Cl bond fission channel, with corresponding photofragments having a kinetic energy distribution peaked well away from zero. This indicates, as in vinyl chloride, that there is a large barrier to the reverse reaction along the C−Cl bond fission coordinate. These studies also find two HCl elimination channels, one fast channel with a kinetic energy distribution of the fragments peaked well away from zero and one slow channel with a kinetic energy distribution peaked closer to zero.

The photodissociation of propargyl chloride at 193 nm was first studied by Kawasaki and co-workers[8] and has been recently reinvestigated by Lin and co-workers.[9] They observe only one C−Cl bond fission channel, with a kinetic energy distribution of the fragments peaked well away from zero, and only one HCl elimination channel, with a kinetic energy distribution of the fragments peaked near zero. Lin and co-workers estimate a branching ratio of C−Cl fission versus HCl elimination of 1:0.19.

Interpretation of the photodissociation dynamics of these three systems is greatly complicated by the possibility of a number of different electronic configurations contributing to the electronic state accessed in each of the molecules' first ultraviolet absorption band. The oscillator strength is carried by $\pi\pi^*_{C=C/C\equiv C}$ character of the transition, but the prompt C−Cl bond fission channel which is important for all these molecules indicates that $n\sigma^*_{C-Cl}$ character could be important in the excited electronic state somewhere along the dissociative reaction coordinate. *Ab initio* calculations on vinyl chloride have further indicated the importance of $\pi\pi^*_{C=C/C\equiv C}$, $n\sigma^*_{C-Cl}$, and $n_{Cl}3s$ Rydberg configurations in this excitation band.[1] It is also likely that there are nearby triplet states which may also mix slightly with these configurations through spin−orbit coupling.

This paper uses the experimental technique of emission spectroscopy to investigate the photodissociation of these molecules. Emission spectroscopy,[10] or resonance Raman spectroscopy of dissociating molecules, affords a probe of the forces on the molecule in the Franck−Condon region of the excited state potential energy surface. These experiments provide a nice complement to photofragment spectroscopy studies, since emission spectroscopy gives information about the portion of the potential energy surface accessed at the beginning of the photodissociation event, while analysis of the

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⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1996.

S0022-3654(95)03106-6 CCC: $12.00 © 1996 American Chemical Society

photofragments provides information about the end products of the dissociation. We use emission spectroscopy to help elucidate the different contributions to the electronic character of the initial excitation. The electronic character in the Franck–Condon region of the excited state surface determines the initial forces on the molecule and therefore influences which vibrational bands appear in the emission spectrum. In this paper, we report the emission spectra of dissociating vinyl, allyl, and propargyl chloride photoexcited at 199 nm, as well as results of our own *ab initio* calculations of the relevant excited states, to determine the varying contribution of $\pi\pi^*$, nσ^*, and $\pi\sigma^*$ electronic configurations to the nominal $\pi\pi^*$ excited state in these three molecules.

Experimental Method

The emission spectra presented in this paper were all collected using the excitation wavelength of 199 nm, which we generate by tripling the output of a Lambda Physik FL3002 dye laser.[11] This dye laser is pumped with the frequency doubled output of a Quantel YG 581-C Nd:YAG laser, operating at 20 Hz. The tripling is done in two steps, by doubling in a potassium dihydrogen phosphate (KDP) crystal and then mixing this doubled light with the residual fundamental in a β-barium borate (BBO) crystal. In this manner we generate up to 350 μJ/pulse of radiation at 199 nm.

Emission experiments are performed in a stainless steel flow cell. The 199 nm light is separated from residual fundamental and second harmonic radiation by dispersion in a Pellin-Broca prism and then directed into the flow cell where it photoexcites the gaseous sample. We flow 0.5–1.5 Torr of sample and flush the side arms with 6 Torr of helium. Vinyl chloride (99.5%) was obtained from Fluka, and allyl (99%) and propargyl chloride (98%) were obtained from Aldrich and used with no further purification. Emitted light is collected at 90° with respect to the direction of propagation of the laser beam. The emitted light is recollimated, passed through a depolarizing wedge, and focused onto the entrance slit of a Spectra-Pro 0.275 m spectrometer. A Milton-Roy 1200 groove/mm holographic grating disperses the emission in first order onto the 18 mm microchannel plate image intensifier of an EG&G 1455B-700-HQ optical multichannel analyzer (OMA). The detector collects a 50 nm wide spectrum for each exposure with a resolution of 75 cm^{-1} at 199 nm. For each exposure of 300 s (6000 laser shots) we gate the image intensifier of the OMA with a pulse synchronized to the laser. For the spectra of vinyl and allyl chloride we summed 25 exposures to obtain spectra averaged over 150 000 laser shots, and for propargyl chloride we summed 100 exposures to obtain a spectrum averaged over 600 000 laser shots.

Theoretical Method

To help determine the character of the excited state(s) accessed in the experiments, we also present *ab initio* electronic structure calculations for vinyl chloride, *gauche*- and *cis*-allyl chloride, and propargyl chloride using the GAUSSIAN 92 program package.[12] The calculations were made using ground state equilibrium geometries calculated at the MP2/6-31G** level of theory for vinyl[13] and allyl chloride[14] and parameters obtained from microwave spectra for propargyl chloride.[15] Configuration interaction with single excitation (CIS) calculations using a 6-311G* basis provide the oscillator strengths for transitions from the ground state and generate a listing of the molecular orbitals which comprise each excited state. Examination of the linear combination of atomic orbitals (LCAOs) contributing to each molecular orbital allows each molecular orbital to be classified with respect to its symmetry and bonding nature. Test calculations were run for *cis*- and *gauche*-allyl chloride using the above basis augmented with two sets of diffuse functions. These results give better vertical excitation energies, but the overall description of the excited state characters are qualitatively the same as those produced with the smaller basis.

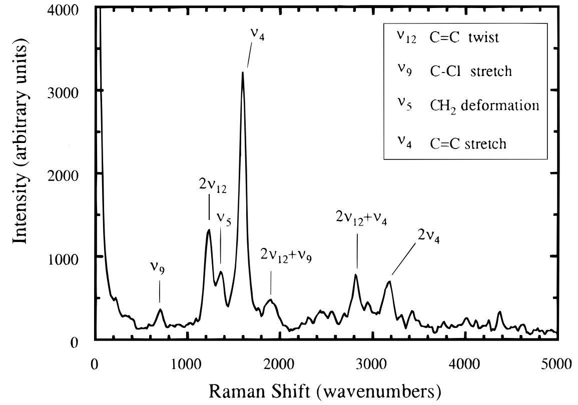

Figure 1. Emission spectrum of dissociating vinyl chloride photoexcited at 199 nm. Vibrational assignments are made according to experimental values reported in ref 16.

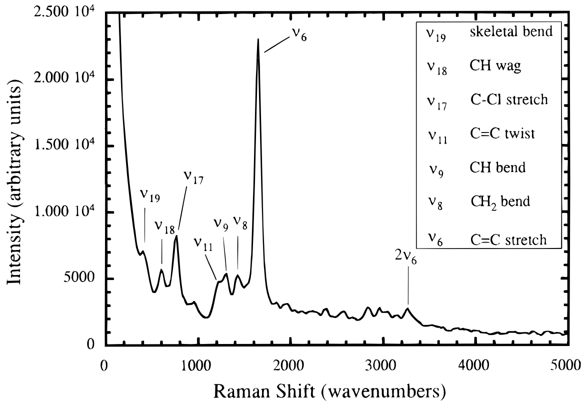

Figure 2. Emission spectrum of dissociating allyl chloride photoexcited at 199 nm. Vibrational assignments are made according to experimental values for the *gauche* conformer reported in ref 17.

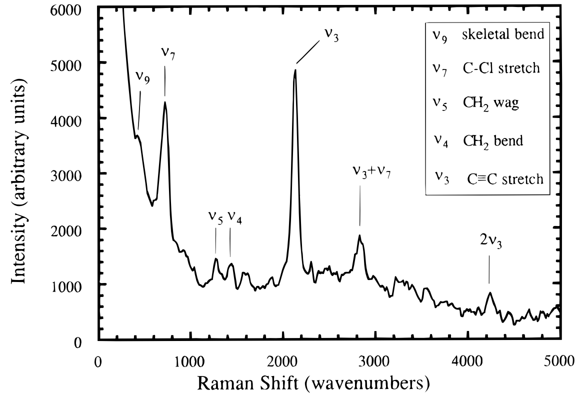

Figure 3. Emission spectrum of dissociating propargyl chloride photoexcited at 199 nm. Vibrational assignments are made according to experimental values reported in ref 18.

Results and Analysis

A. Emission Spectra. Figures 1–3 show the emission spectra of vinyl, allyl, and propargyl chloride, respectively. The most prominent feature in the emission spectra of vinyl and allyl chloride is stretching of the C=C bond, emission to 1 and

TABLE 1: Summary of the Results of the *ab Initio* Calculations; Overall Classification, Oscillator Strength, and Vertical Excitation for the Bright State in Each System; and Components and Coefficients of the CI Expansion for Each State[a]

	vinyl chloride		*cis*-allyl chloride		*gauche*-allyl chloride		propargyl chloride	
classification	$\pi \rightarrow \pi^*$		$\pi \rightarrow \pi^*$		π/n $\rightarrow \pi^*/\sigma^*$		π/n $\rightarrow \pi^*/\sigma^*$	
vertical excitation (eV)	7.8227		8.3827		8.0955		8.3220	
oscillator strength	0.6273		0.5929		0.5775		0.5492	
CI expansion	16 → 17	−0.6848	20 → 22	0.6610	20 → 21	0.6271	18 → 20	−0.4678
					19 → 21	−0.1285	19 → 21	−0.3140
					18 → 21	0.1200	18 → 22	−0.2808
					20 → 22	−0.1004	18 → 24	0.1630
							16 → 20	−0.1610
							15 → 20	−0.1363
							19 → 25	−0.1167

[a] The specific character of each molecular orbital in the expansion is detailed in the text.

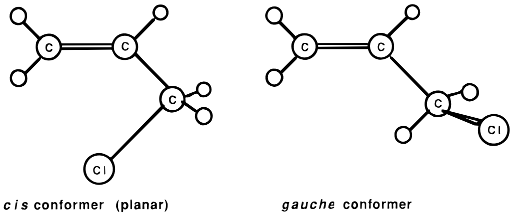

Figure 4. The two conformers of allyl chloride. The *gauche* conformer accounts for approximately 82% of room temperature allyl chloride.

2 quanta of ν_4 and ν_6, respectively. Emission to the C=C stretch mode also appears in combination with C=C twist, $\nu_4 + 2\nu_{12}$, in vinyl chloride. In the emission spectrum of propargyl chloride, the stretching of the C≡C bond, ν_3, is the most prominent feature, slightly stronger than the C−Cl bond stretch, ν_7. The spectra of vinyl and allyl chloride also indicate some twisting motion about the C=C bond. Vinyl chloride shows emission to 2 quanta of C=C twist ($2\nu_{12}$) and combinations of 2 quanta of twist with C−Cl stretch (ν_9) and C=C stretch (ν_4). Emission to 1 quantum, or any odd number of quanta, of this mode is disallowed due to symmetry. Emission to 1 quantum of C=C twist (ν_{11}) is seen in allyl chloride, though emission to twisting modes is less prominent in this molecule. Propargyl chloride shows no twisting motion. All three of these molecules also emit to CH_2 bending or deformation modes.

We can understand the implications of the emission features described above in reference to studies of the first excited state of ethylene. Excitation of a $\pi\pi^*$ transition in ethylene, since it is the simplest π bonded system, can be considered the prototypical $\pi\pi^*$ excitation. Through comparison to the emission spectrum of ethylene, we can identify which features of our emission spectra are indicative of $\pi\pi^*$ electronic character contributing to the excitation. The $\pi\pi^*$ transition in ethylene has been analyzed through consideration of the relevant molecular orbitals by Walsh[19] and later by Mulliken.[20] They each concluded that the $\pi\pi^*$ excited state has an equilibrium geometry which is twisted 90° about the C=C bond with the CH_2 groups deformed to a pyramidal geometry similar to hydrazine. Walsh predicted that the Raman spectrum would show activity in the C=C bond stretching mode, the C=C twist, and various CH_2 bends and deformations. These predictions were confirmed in the resonance Raman spectra of ethylene obtained by Hudson and co-workers.[21,22] The emission spectrum of vinyl chloride presented here, like ethylene, indicates C=C stretching and twisting motion as well as CH_2 bending or deformation, verifying that the excitation has $\pi\pi^*$ character.

Although, like vinyl chloride, the emission spectra of allyl and propargyl chloride evidence the unsaturated carbon−carbon bond stretching (and for allyl chloride twisting as well) modes characteristic of $\pi\pi^*$ electronic character in the excited state, these spectra also include emission to states with 1 and possibly 2 quanta in the C−Cl stretch. This suggests the importance of σ^*_{C-Cl} character in the region of the potential energy surface initially accessed at 199 nm excitation. *Ab initio* calculations by Umemoto and co-workers[1] have indicated the presence of nσ^* and $\pi\sigma^*$ configurations that are close in energy to the first excited state of vinyl chloride but do not contribute significantly in planar geometries. Our own *ab initio* calculations, detailed below, indicate the presence of nσ^* and $\pi\sigma^*$ configurations which do contribute, to varying degrees, to the nominally $\pi\pi^*$ excited states of allyl chloride and propargyl chloride. Therefore, we will analyze the contributions of emission to C−Cl stretching states in the emission spectra with regard to the admixture of nσ^* and $\pi\sigma^*$ character in the Franck−Condon region of the excited electronic state accessed at 199 nm. First, note the following trends. Vinyl chloride shows very little emission to C−Cl stretching, indicating that the forces along the C−Cl bond coordinate are not significant at early times in the photodissociation process, and therefore the Franck−Condon region of the potential energy surface accessed at 199 nm has very little nσ^* or $\pi\sigma^*$ character. In the emission spectrum of allyl chloride, the emission to the C−Cl stretching mode is still much weaker than that to the C=C stretch, but it is significantly stronger than in the spectrum for vinyl chloride. This is indicative of an increased mixing of nσ^* and $\pi\sigma^*$ character into the predominantly $\pi\pi^*$ transition. Finally, the emission spectrum of propargyl chloride evidences emission to C−Cl stretch eigenstates which are comparable in intensity to the C≡C stretch features. Therefore, the initial excitation must promote the molecule to an excited state with considerable nσ^* and $\pi\sigma^*$ character in the Franck−Condon region.

B. *Ab Initio* Results. The results of the *ab initio* calculations for vinyl chloride, *cis*- and *gauche*-allyl chloride (conformers depicted in Figure 4), and propargyl chloride are summarized in Table 1. The table includes the oscillator strength and a characterization of the electronic transition from the ground state for each system. This characterization is based on analysis of the components of the configuration interaction (CI) expansion, also listed in Table 1. Vertical excitation energies from the ground state are also included for reference, but these energies are known to be too high at this level of theory.[23] We present pictures of electron density isosurfaces (Figures 5−7) to help visualize the bonding nature of the excited state molecular orbitals to which transitions are occurring. These results indicate that the excited state reached in vinyl chloride is nearly exclusively $\pi\pi^*_{C=C}$ in the Franck−Condon region, in agreement with the calculations of Umemoto and co-workers.[1] Other low lying states exhibit transitions from $\pi_{C=C}$ and n_{Cl} molecular orbitals to σ^*_{C-Cl} and Rydberg states but do not mix with the nominally $\pi\pi^*$ state in the Franck−Condon region or carry significant oscillator strength.

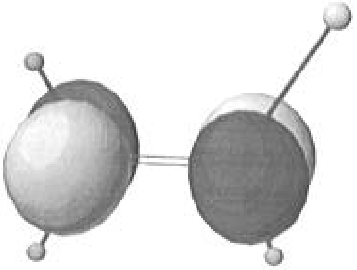

Figure 5. The π^* molecular orbital of vinyl chloride listed as no. 17 in Table 1. The isosurface is plotted where the local electron density has dropped to 0.01 $e^-/Å^3$ (orbital isosurface value = 0.1). This orbital exhibits pure antibonding character along the C═C bond contributed by out-of-plane p orbitals on the carbons.[24]

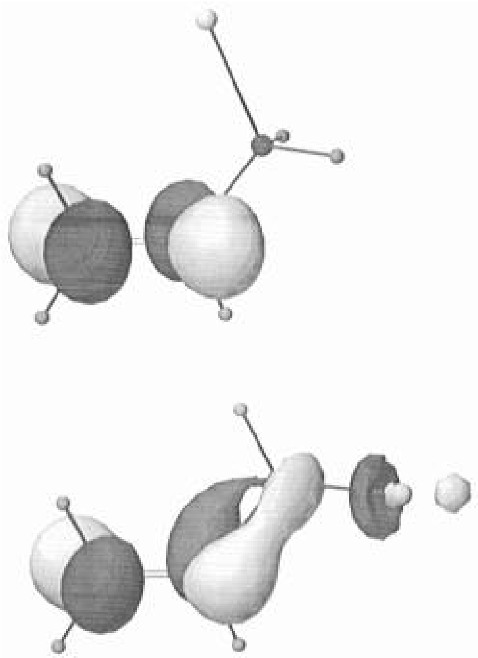

Figure 6. The nominal π^* molecular orbitals of *cis*- (top) and *gauche*- (bottom) allyl chloride listed in Table 1 as nos. 22 and 21, respectively. Note the considerable σ^*_{C-Cl} character of the orbital in the *gauche* conformer. The isosurfaces are plotted where the local electron density has dropped to 0.01 $e^-/Å^3$ (orbital isosurface value = 0.1). Molecular orbital no. 22 for *cis*-allyl chloride (top) exhibits pure antibonding character along the C═C bond like vinyl chloride. Orbital no. 21 for the *gauche* conformer (bottom) again exhibits antibonding character along the C═C bond contributed by out-of-plane p orbitals on the carbons but also has significant antibonding character between the carbon of the CH_2 group and the chlorine atom. This indicates the orbital is best described as containing a combination of π^* and σ^* character.[24]

As suggested by the emission spectra, allyl chloride and propargyl chloride show increased contributions of σ^*_{C-Cl} character to the excited state reached at 199 nm. Allyl chloride exists in two conformations (Figure 4) at room temperature, *cis* and *gauche*, with approximate populations of 18% and 82%, respectively. The electronic transitions are quite different for these two conformations. In *cis*-allyl chloride (Figure 6, top) the electronic state of interest is still pure $\pi\pi^*$ just like vinyl chloride, but in the *gauche* conformer (Figure 6, bottom), the bright state is best described as a mixture that is predominantly $\pi\pi^*$, but also includes $\pi\sigma^*$ and $n\sigma^*$ contributions. This state involves transitions from a π type orbital (molecular orbital 20 in Table 1) and, to a smaller extent, nonbonding orbitals localized on the chlorine atom (orbitals 18 and 19), to a single molecular orbital with significant antibonding character on the C═C bond as well as along the C−Cl bond (orbital 21) as depicted in the bottom frame of Figure 6. There is also a small amount of Rydberg character contributed by orbital 22. Relaxation of symmetry constraints allows the various low lying transitions, similar to those seen in vinyl chloride, to mix with the $\pi\pi^*$ state at the molecular orbital level and also to appear as components of the configuration interaction expansion of the bright state.

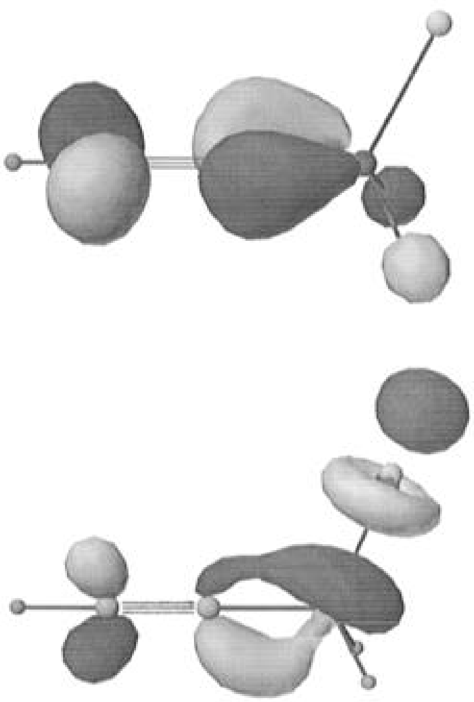

Figure 7. The nominal out-of-plane (top) and in-plane (bottom) π^* molecular orbitals of propargyl chloride listed in Table 1 as nos. 21 and 20, respectively. Note the considerable σ^*_{C-Cl} character of the in-plane orbital. The isosurfaces are plotted where the local electron density has dropped to 0.0081 $e^-/Å^3$ (orbital isosurface value = 0.09). Molecular orbital no. 21 (top) exhibits pure antibonding character along the C≡C bond oriented at a right angle to the molecular plane. Molecular orbital no. 20 (bottom) is similar to that of *gauche*-allyl chloride in that it exhibits antibonding character between the carbon of the CH_2 group and the chlorine atom. This orbital is therefore best described as containing a combination of π^* and σ^* character, with the σ^* character slightly more dominant. Both molecular orbitals 20 and 21 appear in the CI expansion of the bright state for propargyl chloride, making this a state of very mixed character.[24]

Propargyl chloride is a more complex system since transitions involving the two sets of π orbitals which comprise the C≡C bond are possible. Transitions from the π orbital lying in the same plane as the C−Cl bond (orbital 18) have the correct orbital symmetries to mix strongly with the $n\sigma^*$ excitation on the C−Cl bond. Like orbital 21 for *gauche*-allyl chloride, orbital 20 (Figure 7, bottom) has antibonding character along both the C≡C and C−Cl bonds, and orbitals 15 and 16 contribute n_{Cl} character to the expansion. The out-of-plane π orbital (orbital 19) also contributes significantly. Therefore, as with *gauche*-allyl chloride, the bright excitation is best described as mixed, but for this system, the contributions of $n\sigma^*$ and $\pi\sigma^*$ character are nearly equal to that of $\pi\pi^*$ character.

Finally we present results of *ab initio* calculations, in which we twisted the H_2C═ portion of vinyl chloride, in Table 2. We were interested in checking Umemoto's assertion that the $\pi\sigma^*$ configuration mixes with the initially prepared state upon twisting about the C═C bond. This claim was clearly verified in that only a few degrees of distortion (as little as 2°) about this bond led to a mixing of the optically bright $\pi\pi^*$ state with the energetically lower $\pi\sigma^*$ state in vinyl chloride. Between

TABLE 2: Summary of the Results of the *ab Initio* Calculations in Which the $H_2C=$ Group of Vinyl Chloride Is Twisted, and the Coefficients of the CI Expansions for the First Two Singlet Excited States, S_1 and S_2[a]

twist angle (deg)	S_1 CI expansion		S_2 CI expansion	
0	16 → 19	0.4388	16 → 17	−0.6848
	16 → 20	−0.4521		
4	16 → 17	0.1819	16 → 17	−0.6543
	16 → 18	0.4852	16 → 18	0.1532
	16 → 19	0.4113		
8	16 → 17	−0.3284	16 → 17	−0.5919
	16 → 18	−0.4174	16 → 18	0.2641
	16 → 19	−0.3953	16 → 19	0.1799
12	16 → 17	0.4353	16 → 17	0.5160
	16 → 18	0.3421	16 → 18	−0.3302
	16 → 19	0.3648	16 → 19	−0.2551
25	16 → 17	0.6104	16 → 17	0.2883
	16 → 18	−0.1694	16 → 18	0.4037
	16 → 19	0.2168	16 → 19	−0.3700
40	16 → 17	0.6669	16 → 17	−0.1359
			16 → 18	−0.4337
			16 → 19	−0.3476

[a] In planar geometry, S_1 is purely nσ^* and S_2 is $\pi\pi^*$, but twisting results in mixing and eventual reordering of the states.[25]

20° and 30° of twist, these two states experience their strongest interaction and form an avoided crossing, with the lower energy adiabat evolving to a $\pi\pi^*$ configuration past the crossing region. This is easily seen in Table 2 by comparing the configuration interaction expansion coefficients for the two lowest lying singlet states. As the $H_2C=$ group is twisted, $\pi\pi^*$ (orbitals 16 → 17) character from S_2 mixes with S_1 until S_1 becomes pure $\pi\pi^*$ and S_2 becomes $\pi\sigma^*$.

Discussion

The emission spectra in conjunction with our *ab initio* calculations give us a good understanding of the region of the potential energy surface initially accessed in these electronic transitions. The emission spectra exhibit a large difference in the relative intensity of the emission to C−Cl stretching eigenstates, indicating a variation in the contributions of σ^*_{C-Cl} electronic character to the excited state in the Franck−Condon region. The preceding Results and Analysis section detailed how the $\pi\pi^*$ electronic character which carries the oscillator strength in these transitions mixes with other electronic configurations, most notably nσ^* and $\pi\sigma^*$, in the region of the potential energy surface accessed at 199 nm, resulting in C−Cl antibonding forces in the Franck−Condon region, particularly in *gauche*-allyl chloride and propargyl chloride. Now we will consider how the symmetry of the molecular orbitals involved in the electronic configurations helps determine the extent of their configuration interaction contribution to these nominally $\pi\pi^*$ excited states. We will conclude by analyzing our results with respect to the photofragment studies on allyl, vinyl, and propargyl chloride to understand how the variations in the electronic character of the potential energy surface may influence the branching to the end products of the photodissociation.

A. Symmetry Effects on the Mixing of $\pi\pi^*$, nσ^*, and $\pi\sigma^*$ Configurations. The emission spectrum and our *ab initio* calculations demonstrate that the excitation in vinyl chloride in its first absorption band is virtually pure $\pi\pi^*$ in character. We now consider the symmetries of the relevent molecular orbitals to analyze why the coupling between the $\pi\pi^*$ and nσ^* electronic configuration is particularly weak in this molecule (coupling with the $\pi\sigma^*$ configuration is forbidden for planar geometries), resulting in nearly pure $\pi\pi^*$ character in the bright transition for vinyl chloride at this excitation wavelength. The π bond in vinyl chloride is composed of p orbitals perpendicular to the molecular plane, and has a″ symmetry. The π^* orbital, composed of similar p orbitals, has a″ symmetry, thus the $\pi\pi^*$ excited electronic configuration has A′ symmetry. The chlorine atom lies in the plane of symmetry of vinyl chloride, so the relevant n and σ^* orbitals are each of a′ symmetry and the symmetry of the nσ^* excited electronic configuration is also A′. These two electronic configurations, having the same overall symmetry, mix and split to form two adiabatic surfaces of mixed electronic character. However, the mixing of these two electronic configurations is weakened because of the difference in the symmetries of the individual orbitals involved in the two excitations, a′, a′ versus a″, a″. Waschewsky *et al.*[26] have pointed out that the configuration interaction matrix elements between two states where there is a lack of conservation of individual orbital symmetry (the lower orbital reverses symmetry from a″ to a′ and the antibonding orbital from a″ to a′ in the case of chloroacetone discussed in ref 26) are anomalously small. Although in that work they were primarily interested in the configuration interaction splitting at a reaction barrier formed from an avoided configuration crossing, the same argument applies here to the configuration mixing to produce a potential energy surface with mixed electronic character in the Franck−Condon region. The symmetry of the $\pi\sigma^*$ transition is A″, and therefore this configuration cannot mix at all with the bright $\pi\pi^*$ transition for planar geometries. Thus, for planar geometries overall symmetry dictates that the $\pi\sigma^*$ configuration cannot mix with the $\pi\pi^*$ bright electronic character and consideration of individual orbital symmetry indicates that the admixture of nσ^* character should be very weak in the Franck−Condon region of the accessed $\pi\pi^*$ potential energy surface. The emission spectrum indicates, however, that the photoexcited molecule experiences twisting forces about the C=C bond which will rapidly distort the plane of symmetry. Our calculations show that twisting motion causes the rapid admixture of $\pi\sigma^*$ character into the excited electronic state.

In the *gauche* conformer of allyl chloride, the plane of symmetry is broken, resulting in a stronger interaction between the $\pi\pi^*$ and nσ^* electronic configurations and allowing mixing with the $\pi\sigma^*$ configuration as well. This yields an initial excitation to an electronic state which contains some nσ^* and $\pi\sigma^*$ character as is demonstrated by our *ab initio* calculations. The emission spectrum, which should mainly reflect the dynamics of the dominant *gauche* conformer, shows significant C−Cl motion. The *cis* conformer, which forms a minor contribution at room temperature, maintains a plane of symmetry, and just as with vinyl chloride, the $\pi\pi^*$ and nσ^* configurations have the same overall symmetry, A′, but the individual orbitals involved in these two configurations have different symmetries. The $\pi\sigma^*$ configuration is A″ and therefore cannot mix with the $\pi\pi^*$. Our calculations confirm that for the *cis* conformer the electronic character of the potential surface accessed is nearly pure $\pi\pi^*$ in character in the Franck−Condon region.

For planar geometries of vinyl and *cis*-allyl chloride, the interaction between the $\pi\pi^*$ and nσ^* electronic configurations involved in the photoexcitation of vinyl and allyl chloride can be more formally treated by an argument that closely follows that of Silver.[27] We consider the interaction of two electronic configurations in the Franck−Condon region. The electronic configuration representing the $\pi\pi^*$ excitation can be written symbolically as $\Psi_R = \{...(n_{Cl})^2(\pi_{C=C})^1(\sigma^*_{C-Cl})^0(\pi^*_{C=C})^1\}$, and the configuration representing nσ^* excitation can be written symbolically as $\Psi_P = \{...(n_{Cl})^1(\pi_{C=C})^2(\sigma^*{}_{C-Cl})^1(\pi^*{}_{C=C})^0\}$. Configuration interaction matrix elements mix and split these two electronic configurations to form two adiabatic potential energy surfaces of mixed electronic character. In this two-state model, with no orthonormality assumed between reactant and product molecular orbitals or between Ψ_R or Ψ_P, the expression for the energy eigenvalues of these two states is

$$E = \{{}^1/_2(\alpha + \gamma) - \beta S \pm [{}^1/_4(\alpha - \gamma)^2 + \beta^2 - \beta S(\alpha + \gamma) + \alpha\gamma S^2]^{1/2}\}(1 - S)^{-1} \quad (1)$$

in which α is the energy of the unperturbed state Ψ_R, γ is the energy of the unperturbed state Ψ_P, S is the overlap integral, $\langle\Psi_R|\Psi_P\rangle/C$, and β is the exchange energy, $\langle\Psi_R|H|\Psi_P\rangle/C$; C corrects for unnormalized wave functions. The mixing of the two configurations is determined by the S and β terms.[28] However, for the case where the symmetries of the individual orbitals in the two separate excitations are orthogonal, such as in the cases of vinyl or *cis*-allyl chloride, the overlap integral S, as well as all one-electron β integrals, is zero. This leaves only the two-electron integrals in the β term:[29]

$$\beta = 2\left\langle n_{Cl}(1)\pi_{C=C}(2)\left|\frac{e^2}{r_{12}}\right|\sigma^*{}_{C-Cl}(1)\pi^*{}_{C=C}(2)\right\rangle - \left\langle n_{Cl}(1)\sigma^*{}_{C-Cl}(2)\left|\frac{e^2}{r_{12}}\right|\pi_{C=C}(1)\pi^*{}_{C=C}(2)\right\rangle \quad (2)$$

Thus, there is very little mixing of the two electronic configurations to form the two resultant adiabatic surfaces and the bright surface accessed in these molecules will be nearly pure $\pi\pi^*$ character in the Franck–Condon region. For *gauche*-allyl chloride, the plane of symmetry is broken, and these integrals do not all go to zero, resulting in greater mixing of the two electronic configurations in the two resultant adiabats. Therefore, in *gauche*-allyl chloride the bright surface as some nσ^* character in the Franck–Condon region.

The photoexcitation of propargyl chloride involves a $\pi\pi^*$ excitation on a C≡C bond and the mixing of this excitation with nσ^* and $\pi\sigma^*$ electronic configurations. This is certainly a different case than the excitations in vinyl and allyl chloride, yet we can understand the mixing of these configurations in propargyl chloride in a similar manner. The emission spectrum of propargyl chloride shows emission to C–Cl stretching eigenstates with nearly equal intensity to that of emission to the C≡C stretch. Our *ab initio* calculations confirm that this excitation involves a state of mixed $\pi\pi^*$, nσ^*, and $\pi\sigma^*$ character. There are two π orbitals which contribute to this $\pi\pi^*$ state, one in the plane of the molecule and one perpendicular to the plane. The π orbital in the plane has a′ symmetry, and excitation from this orbital to an a′ symmetry π^* orbital has the correct individual orbital symmetry to mix with the nσ^* transition, resulting in significant nσ^* character in the initial excitation.

B. Ramifications for the Branching between Available Photofragment Channels. The emission spectra help us to understand the nature of the excited state potential energy surface in the Franck–Condon region, which can in some cases influence the branching to available product channels. For these three molecules C–Cl fission occurs following the passage over the barrier formed by the avoided crossing of the approximately diabatic $\pi\pi^*$ and nσ^* states. Although $\pi\sigma^*$ character contributes to the initial excitation in *gauche*-allyl chloride and propargyl chloride, calculations by Umemoto and co-workers[1] on vinyl chloride show that the $\pi\sigma^*$ state is bound, so it is unlikely that this state leads to C–Cl fission in this set of molecules. Umemoto and co-workers instead speculate that crossing to this state assists eventual internal conversion to the ground state resulting in the HCl elimination channel in vinyl chloride. The $\pi\pi^*$ and nσ^* electronic configurations mix and split to form the resulting adiabatic potential energy surfaces, and the extent of the mixing helps determine both the height of the barrier formed by the avoided crossing of two different electronic configurations and the splitting between the two potential energy surfaces at the barrier. Greater interaction leads to a larger splitting of the resulting adiabatic surfaces and therefore a lower barrier to passage along the lower adiabat. Conversely, weaker interaction of these two configurations results in a larger barrier. Experimental work in our laboratory indicates that in cases of weak coupling of the relevant configurations, bond fission is further suppressed by nonadiabatic transitions at the barrier and subsequent recrossing and return to the Franck Condon region.[25]

With these ideas in mind, and in light of recent crossed laser–molecular beam experiments of Myers and co-workers[6] which compare the branching between C–Cl bond fission and HCl elimination channels between vinyl and allyl chloride, we can determine if the trends of the relative contribution of nσ^* character in the Franck–Condon region follow the trends of the experimental results. Our emission spectra and our calculations show that the initial excitation in *gauche*-allyl chloride (the dominant conformer) has some nσ^* character. This indicates some coupling between the $\pi\pi^*$ and nσ^* electronic configurations. In contrast, the emission spectrum and calculations for vinyl chloride indicate virtually no nσ^* character in the initial excitation, indicating very little coupling of the $\pi\pi^*$ and nσ^* electronic configurations. These results suggest that allyl chloride should show increased branching to the C–Cl bond fission channel relative to vinyl chloride. The recent experimental results of Myers and co-workers[6] show a branching ratio of C–Cl fission to HCl elimination of 1:0.11 which is indeed larger than the ratio of 1:1 that had been previously measured for vinyl chloride by Umemoto and co-workers[1].

Lin and co-workers have recently reinvestigated the photodissociation of propargyl chloride excited at 193 nm,[9] and they again find a branching ratio that strongly favors C–Cl fission, a ratio of 1:0.19 for C–Cl fission:HCl elimination. This system cannot be compared directly with allyl chloride, since it involves a C≡C bond and the HCl elimination pathway is likely to be strongly influenced by this difference. Analysis of the admixture of nσ^* and $\pi\pi^*$ character in the Franck–Condon region and consideration of nonadiabatic effects at the barrier, if there is one, to C–Cl bond fission may not be the dominant factors in determining the HCl elimination versus C–Cl fission branching.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. NSF CHE 9307500. We thank J. E. Stevens for helpful discussions and S. Lin for providing us with a preprint of his work in ref 9 prior to publication. L.J.B. would like to thank Jim Kinsey for allowing her to do undergraduate research with him and Bob Field and for first explaining the Franck–Condon principle to her in a hallway at MIT back in 1980.

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JP9531063