

Emission Spectroscopy of Dissociative Allyl Iodide and Allyl Alcohol Excited at 199.7 nm

B. F. Parsons, D. E. Szpunar, and L. J. Butler*

The James Franck Institute and Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Received: June 21, 2000; In Final Form: September 12, 2000

We have investigated the emission spectroscopy of allyl iodide, $\text{CH}_2=\text{CHCH}_2\text{I}$, and allyl alcohol, $\text{CH}_2=\text{CHCH}_2\text{OH}$, excited at 199.7 nm. Ab initio calculations at the configuration interaction with single excitation (CIS) level indicate that the excited state accessed near 200 nm in allyl iodide has mixed electronic character with contribution from a $\pi \rightarrow \text{Rydberg}(16)$ configuration, a $\pi_{\text{C}=\text{C}}/\text{n}_\text{I} \rightarrow \sigma^*_{\text{C}-\text{I}}/\pi^*_{\text{C}=\text{C}}$ configuration, and a $\pi \rightarrow \text{Rydberg}(20)$ electronic configuration (where we have given the number of the Rydberg molecular orbital in parentheses). The emission spectrum is dominated by activity in the CH_2 wag and the $\text{C}=\text{C}$ stretch, reflecting the dynamics of the molecule in the Franck–Condon region of the excited state. The emission spectrum along with the ab initio calculations on the two conformers of allyl alcohol present at room temperature allow us to assign the transition at 200 nm to be mixed $\pi\pi^*$ character and $\pi \rightarrow \text{Rydberg}$ in character.

I. Introduction

In emission spectroscopy, we excite a molecule on resonance to some dissociative excited state.^{1–3} The shape of the excited state potential typically differs from that of the ground state, so the electronically excited molecules feel a force driving them away from the equilibrium geometry of the ground state. Molecules excited to a repulsive or strongly predissociated electronic state proceed to dissociate on a picosecond or subpicosecond time scale; however, there is a competition between dissociation and emission of a photon during dissociation (typically a visible/ultraviolet photon from the electronic dipole transition of a small fraction of the dissociating molecules back to the ground electronic state) that results in a small quantum yield of emitted photons from the group of dissociative molecules. The emission spectrum reflects the Franck–Condon overlap of the dissociative wavefunction in the excited state with particular excited vibrational state(s) of the ground electronic state (perhaps corresponding to a bond stretching or twisting of some bond angle in the excited state).

Allyl iodide is frequently used in the formation of the allyl radical either through pyrolysis or photolysis at 248⁴ or 266 nm.^{5–7} Therefore, numerous studies of the allyl radical may be found in the literature while there are relatively few reports on the photochemistry of allyl iodide itself. The absorption spectrum of allyl iodide near 200 nm has been presented twice in the literature. Boschi and Salahub⁸ observed the vapor phase spectrum of allyl iodide and found a strong absorption at 200 nm with a shoulder slightly to the red of this peak. Their paper tentatively assigns the $\text{n}_\text{I}\pi^*_{\text{C}=\text{C}}$ transition of allyl iodide to the shoulder but does not give an assignment of the peak at 200 nm. Worrell⁹ also observed an absorption peak near 200 nm and two higher energy peaks near 190 and 175 nm. The transitions at 200 and 190 nm were assigned to $\text{n}_\text{I}\pi^*_{\text{C}=\text{C}}$ transitions from the nonbonding iodine p orbitals to the $\pi^*_{\text{C}=\text{C}}$ orbital while the transition near 175 nm was assigned as $\pi_{\text{C}=\text{C}}/\pi^*_{\text{C}=\text{C}}$.

Barnes and Holroyd¹⁰ used a Hg lamp to study the photolysis of allyl chloride, allyl bromide, and allyl iodide in Ar matrices. Using IR spectroscopy, they determined the primary products of the photolysis to be allene and HX (X = Cl, Br, I). Camaggi et al.¹¹ studied the formation of allyl arenes in solution through the photolysis of allyl iodide in aromatic solvents using a Hg

lamp. Baklanov et al.¹² used femtosecond pump–probe spectroscopy to study the excited-state lifetime of allyl iodide at 7.8 eV. In two other studies^{13,14} the photodissociation of allyl iodide to give iodine atoms in the ground and spin–orbit excited state was examined. Baklanov et al. studied the dissociation of allyl iodide using the third harmonic of an Nd:YAG laser (355 nm) and using vibrational overtone excitation ($\text{C}-\text{H}$, $\nu = 5$) giving iodine as the primary product.¹³ In a separate study, the dissociative lifetime of allyl iodide was determined using vibrational overtone excitation ($\text{C}-\text{H}$, $\nu = 6$).¹⁴ Very recently, Arnold et al. found dissociation of allyl iodide at 266 nm gave I $^2\text{P}_{1/2}$.⁷

Getty et al. investigated the emission spectroscopy of the allyl radical and allyl iodide.^{5,6} They presented the emission spectrum of allyl iodide at 224.63 nm⁵ and 237.11, 237.29, and 240.51 nm.⁶ The emission spectra taken at 237.11, 237.29, and 240.51 nm all show the most intense band to be ν_{18} , an out-of-plane deformation of the vinyl hydrogen. In all three low-energy spectra, ν_6 ($\text{C}=\text{C}$ stretch), ν_{19} (skeletal bending), and ν_{10} (methylene CH_2 wag) have roughly comparable intensity. Finally, a low-intensity peak is observed at ν_{20} (skeletal bending).⁶ At 224.63 nm, the emission spectrum has similar features to the spectra taken at lower excitation energy, but with different relative intensities. In particular the $\text{C}=\text{C}$ stretch, ν_6 , is the most intense at 224.63 nm, just stronger than ν_{18} .⁵

We are not aware of any published absorption spectrum of allyl alcohol extending to the 200 nm region. The only study of the photochemistry of allyl alcohol known to the authors was by Shimo et al.¹⁵ who investigated the relative yields of allyl radical formation through 193.3 nm photolysis from several alkenes and substituted alkenes including allyl alcohol.

Previous work in our lab investigated the excited state accessed at 199 nm in allyl chloride as well as two related molecules, vinyl chloride and propargyl chloride.¹⁶ CIS calculations using Gaussian 92 showed the excitation in all three of the related molecules has some $\pi\pi^*$ electronic character. Allyl chloride exists as two conformers at room temperature, *cis* (18%) and *gauche* (82%). Ab initio calculations on *cis*-allyl chloride indicated the excited state accessed at 199 nm was purely $\pi\pi^*$ in character. The other conformer, *gauche*-allyl chloride, showed a $\pi\pi^*$ excited state with modest contributions from no^* and $\pi\sigma^*$ electronic configurations. The most intense band observed

TABLE 1: Experimental/MP2 Optimized Z-matrix of Allyl Iodide and the (sp,sc) and (ac,-sc) Conformers of Allyl Alcohol

Allyl Iodide	(sp,sc) Allyl alcohol	(ac,-sc) Allyl alcohol
C	C	C
C 1 1.348	C 1 1.334	C 1 1.336
C 2 1.478 1 123.0	C 2 1.500 1 124.7	C 2 1.495 1 125.3
H 3 1.096 2 110.6 1 0.0	O 3 1.425 2 113.6 1 22.0	O 3 1.432 2 112.2 1 122.0
H 3 1.096 2 110.6 1 -123.882	H 4 1.029 3 102.8 2 62.0	H 4 1.029 3 102.8 2 -62.0
I 3 2.147 2 111.7 1 118.688	H 3 1.112 2 111.3 4 124.532	H 3 1.106 2 112.1 1 -119.52
H 2 1.081 1 120.0 3 180.0	H 3 1.108 2 111.7 4 -118.047	H 3 1.110 2 111.9 1 0.0
H 1 1.081 2 120.0 3 0.0	H 1 1.101 2 119.8 3 180.0	H 1 1.101 2 119.9 3 180.0
H 1 1.081 2 120.0 3 180.0	H 2 1.103 1 119.0 3 180.0	H 2 1.101 1 118.9 3 180.0
	H 1 1.102 2 119.0 3 0.0	H 1 1.103 2 119.9 3 0.0

in the emission spectrum of allyl chloride excited at 199 nm is the C=C stretch. Less intense bands assigned as C-Cl stretch appeared in the spectra, consistent with the electronic character of the excited state of *gauche*-allyl chloride. We apply the same technique in the work reported here to study the Franck-Condon region of the excited state of allyl iodide and allyl alcohol accessed near 200 nm. In section II we give a brief description of our experimental setup. Section III describes the ab initio calculations performed on the room temperature conformers of allyl iodide and allyl alcohol. Section IV gives a summary of our experimental and theoretical results. The discussion section first compares our emission spectrum of allyl iodide excited at 199.7 nm and the previous emission spectra of allyl iodide^{5,6} excited between 225 and 240 nm with our ab initio results. We then compare the emission spectrum of allyl alcohol excited at 199.7 nm with our ab initio calculations.

II. Experimental Section

The apparatus used in these experiments has been discussed previously.^{16,17} Briefly, we generate the excitation light by Raman shifting the fourth harmonic of an injection-seeded Nd:YAG laser (Continuum Powerlite 9020) in 50 psi of H₂. An input pulse of about 100 mJ at 20 Hz gives approximately 100 μ J of light at 199.7 nm (the third anti-Stokes line). Between 500 and 1 Torr partial pressure of sample passes into the center of a flow cell while approximately 4 Torr of He buffer gas flows continuously through the sidearms of the cell to prevent accumulation of material on the cell windows. The emission from dissociating molecules is imaged into a 0.275 m spectrometer (Acton SpectraPro 275, slit width 3 μ m) and dispersed with a 2400gr/mm holographic grating (Milton Roy) onto an optical multichannel analyzer (EG&G PARC 1456B-990-HQ). With this experimental configuration, our resolution is about 25 cm⁻¹ fwhm.

Allyl iodide (98%) and allyl alcohol (99+%) were obtained from Aldrich and used without further purification. We recorded the vapor phase absorption spectrum of allyl alcohol between 190 and 300 nm. Enough allyl alcohol was placed in a cuvette to cover the bottom. An HP 8453 diode-array UV-visible spectrophotometer was then used to record the absorption spectrum of the room-temperature sample (vapor pressure = 18.5 Torr at 298 K, path length = 1 cm).

III. Ab Initio Calculations

As with allyl chloride, both allyl iodide and allyl alcohol may exist in several conformations at room temperature. The room temperature conformers of allyl iodide and allyl alcohol are shown in Figure 1. Allyl iodide has two possible conformers, *cis* with the iodine in the C=C-C plane and *gauche* with the iodine out of the C=C-C plane. At room temperature, *gauche*-

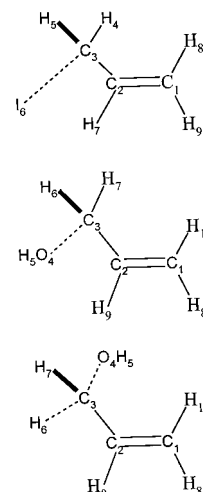


Figure 1. Room temperature conformers of allyl iodide and allyl alcohol. The *gauche* conformer of allyl iodide (top) is the only conformer with significant population. Allyl alcohol exists as two conformers (sp,sc), shown in the bottom, accounts for about 57% of the room-temperature population while the (ac,-sc) conformer, middle of figure, makes up about 43% of the population. We give the MP2 optimized Z-matrix used in our CIS calculations for each of these molecules in Table 1.

allyl iodide is the only conformer with any significant population.¹⁸ Allyl alcohol has six principal conformers, but at room temperature the (sp,sc) conformer (Figure 1 bottom) accounts for 57% of the total population and the (ac,-sc) conformer (Figure 1 middle) makes up 43% of the total population (we have used the notation of ref 19). In the (ac,-sc) conformer one of the allylic hydrogens is in the C=C-C plane, the O is 122° out of the C=C-C plane, and the hydroxyl H is 62° out of the C-C-O plane. For the (sp,sc) conformer none of the allylic hydrogens nor the hydroxyl group lie in the C=C-C plane.¹⁹

We performed ab initio calculations using the Gaussian 98²⁰ package to aid in understanding the electronic character of the excited state accessed near 200 nm. The calculations on allyl iodide required the use of an effective core potential for iodine. We use the LANL2DZ (Hay-Wadt)²¹ basis set augmented with diffuse sp²² and p²³ polarization functions on the H atoms; diffuse sp²² and d²³ polarization functions on the C atoms; and diffuse s and p, and d and f polarization functions on the I atom.²⁴ Using this basis set, we used the experimental²⁵ ground state geometry of allyl iodide but optimized the C-H and C-I bond lengths and the out-of-plane dihedral angles in the CH₂I moiety at the MP2 level before performing CIS calculations. The missing dihedral angles in the experimental¹⁹ ground state geometries of both allyl alcohol conformers were optimized at

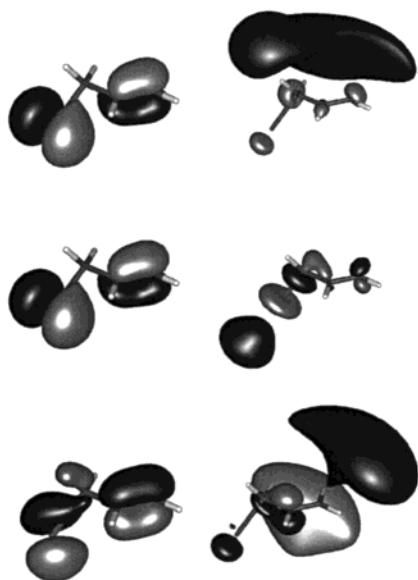


Figure 2. Electronic configurations corresponding to the bright state near 200 nm of *gauche*-allyl iodide. The top configuration with a CI weight 0.39 is $\pi \rightarrow \text{Rydberg}(16)$. The middle configuration, with a CI weight of 0.367 31 is $\pi_{\text{C}=\text{C}}/\text{n}_1 \rightarrow \sigma^*_{\text{C}-\text{I}}/\pi^*_{\text{C}=\text{C}}$. Finally, the bottom configuration with a CI weight of -0.20 corresponds to a $\pi \rightarrow \text{Rydberg}(20)$ excitation. The π orbital involved in the bottom electronic configuration differs from that in the other two by the orientation of the I lone pair.

the MP2/6-311+G** level, restricting H_{7-10} in the (ac, -sc) conformer and H_{8-10} in the (sp,sc) conformer to lie in the molecular plane. The experimental/MP2 optimized Z-matrix used in these calculations is given in Table 1. Table 2 gives the vertical excitation energies and oscillator strengths at the CIS level (configuration interaction with single excitation) for the (sp,sc) and (ac, -sc) conformers of allyl alcohol and for *gauche*-allyl iodide. We have also included the CI weighting coefficients²⁶ for the orbitals participating in the electronic transition as well as an assignment of the individual orbitals. Figures 2, 3, and 4 present images of the orbitals participating in the electronic transition using the molecular visualization package Molden.²⁷

IV. Results

A. Allyl Iodide. The emission spectrum of allyl iodide excited at 199.7 nm, obtained after careful cleaning and baking out of our flow cell (to reduce I_2 contamination), appears in Figure 5. The feature, at 1135 cm^{-1} , is assigned as ν_{10} (methylene CH_2 wag) which has a literature value of 1150 cm^{-1} .²⁸ The feature near 2270 cm^{-1} is assigned as $2\nu_{10}$. The intense feature, located at 1610 cm^{-1} , is assigned as ν_6 ($\text{C}=\text{C}$ stretch) which has a literature value of 1632 cm^{-1} .²⁸ The first several lines in the spectrum are spaced by about 200 cm^{-1} . The *cis* conformer of allyl iodide has a vibration with a frequency of 197 cm^{-1} , ν_{20}

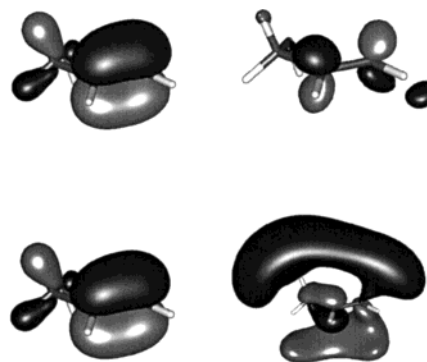


Figure 3. Electronic configurations corresponding to the bright state near 200 nm in the (sp,sc) conformer of allyl alcohol. The top configuration corresponds to a $\pi_{\text{C}=\text{C}}\pi^*_{\text{C}=\text{C}}$ excitation with a CI weight of 0.44. The bottom electronic configuration, with a CI weight of -0.38 , has $\pi \rightarrow \text{Rydberg}(20)$ character.

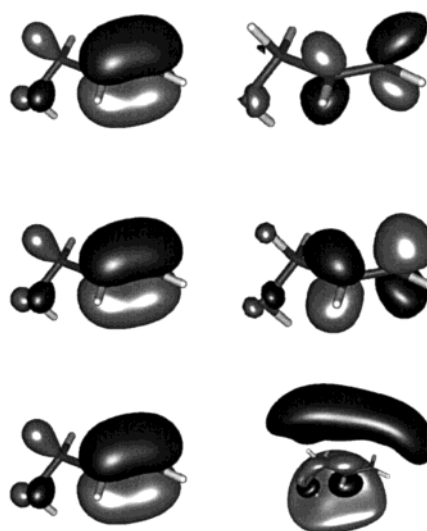


Figure 4. Electronic configurations corresponding to the bright state near 200 nm in the (ac, -sc) conformer of allyl alcohol. The top configuration corresponds to a $\pi_{\text{C}=\text{C}}\pi^*_{\text{C}=\text{C}}$ excitation with a CI weight of 0.52. The middle electronic configuration, with a CI weight of -0.23 , has $\pi_{\text{C}=\text{C}}\pi^*_{\text{C}=\text{C}}$ character but involves a different π^* orbital. The final electronic configuration, with a CI weight of 0.22, corresponds to a $\pi \rightarrow \text{Rydberg}(20)$ transition.

(skeletal bend).²⁸ But since the *gauche* conformer is the dominant conformer at room temperature, it is unlikely that these features arise from *cis*-allyl iodide. However, the vibrational frequency of I_2 is about 210 cm^{-1} .²⁹ The initial features are therefore assigned to residual I_2 background, as is the noticeable nonzero background of the entire spectrum which remains even after careful cleaning of the cell.

Several weak features are present in the spectrum which we assign as follows. The peak at 1370 cm^{-1} is a combination band

TABLE 2: Results of CIS Calculations Using Gaussian 98 for Allyl Iodide and the Two Room Temperature Conformers of Allyl Alcohol

	<i>gauche</i> allyl iodide	(sp, sc) allyl alcohol	(ac, -sc) allyl alcohol
vertical excitation (eV)	7.06	7.57	7.71
oscillator strength	0.53	0.46	0.58
orbital assignment	$\pi \rightarrow \text{Rydberg}(16)$ $\pi_{\text{C}=\text{C}}/\text{n}_1 \rightarrow \sigma^*_{\text{C}-\text{I}}/\pi^*_{\text{C}=\text{C}}$ $\pi \rightarrow \text{Rydberg}(20)$	$\pi \rightarrow \pi^*$ $\pi \rightarrow \text{np}$	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $\pi \rightarrow \text{Rydberg}(20)$
CI expansion contribution/ weighting coefficient	15 \rightarrow 16; 0.39 15 \rightarrow 19; 0.37 13 \rightarrow 20; -0.20	16 \rightarrow 21; 0.44 16 \rightarrow 20; -0.38	16 \rightarrow 21; 0.52 16 \rightarrow 28; -0.23 16 \rightarrow 20; 0.22

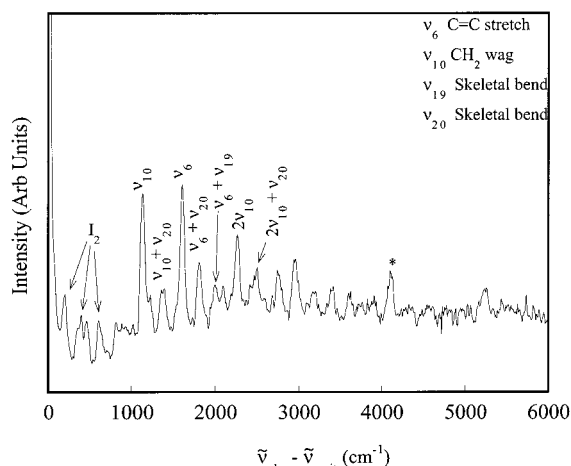


Figure 5. Emission spectrum of allyl iodide excited at 199.7 nm. The values of the vibrational frequencies used in the assignments are taken from ref 27. The asterisk indicates residual 218 nm photons from the second anti-Stokes line produced during the Raman shifting of the 266 nm light in H₂.

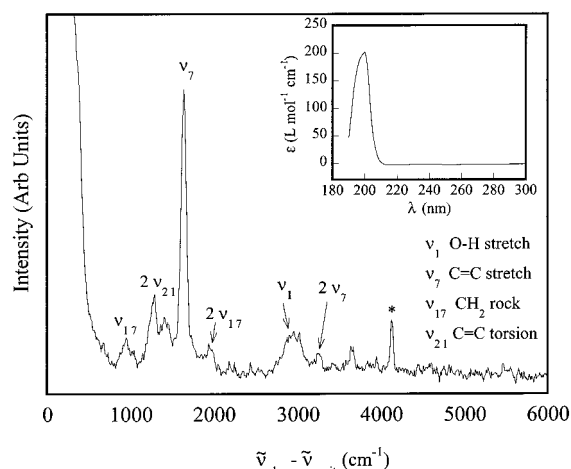


Figure 6. Emission spectrum of allyl alcohol excited at 199.7 nm. The values of the vibrational frequencies used in the assignments are taken from ref 29. We number the vibrational normal modes from the highest frequency (ν_1) to lowest frequency (ν_{24}). The inset is the absorption spectrum of allyl alcohol between 190 and 300 nm. The peak absorption at 200.0 nm has an extinction coefficient $\epsilon = 201.8$ L mol⁻¹ cm⁻¹. The asterisk indicates residual 218 nm photons from the second anti-Stokes line produced during the Raman shifting of the 266 nm light in H₂.

of the methylene CH₂ wag and a skeletal motion, $\nu_{10} + \nu_{20}$. The 1810 cm⁻¹ feature is a combination band of C=C stretch with skeletal bending, $\nu_6 + \nu_{20}$. The feature at 2000 cm⁻¹ is another combination band, $\nu_6 + \nu_{19}$, C=C stretch plus skeletal bend. The feature at 2495 cm⁻¹ is spaced 225 cm⁻¹ away from the 2270 cm⁻¹ feature previously assigned as $2\nu_{10}$. This spacing is 7 cm⁻¹ less than the literature value for the frequency of ν_{20} . We therefore assign this peak as $2\nu_{10} + \nu_{20}$. The assignment of the few remaining peaks at larger shifts from the laser line is very ambiguous so we do not give these except for the feature at 4120 cm⁻¹ (indicated with an asterisk). This is residual 218 nm radiation, the second anti-Stokes line produced during the Raman shifting of the 266 nm light in H₂.

B. Allyl Alcohol. No absorption spectrum for allyl alcohol near 200 nm is reported in the literature. Thus, we recorded the UV absorption spectrum shown in Figure 6 (inset). The peak absorption, at 200 nm, dominates the spectrum; this is the electronic state we access in this study. Figure 6 shows the

emission spectrum of allyl alcohol excited at 199.7 nm. The laser line is noticeably broader in Figure 6 than in Figure 5. This is due to scattering from material which accumulated on the windows over the course of the experiment. The most intense feature in Figure 6, appearing at about 1640 cm⁻¹, is easily assigned to the C=C stretch, ν_7 , with a literature frequency of 1646 cm⁻¹.³⁰ A very weak feature around 3255 cm⁻¹ is $2\nu_7$, two quanta of the C=C stretch. A small peak appears at 950 cm⁻¹, which we assign as the CH₂ rock, ν_{17} . The literature value for the CH₂ torsional frequency is 642 cm⁻¹.³⁰ Thus, we assign the peak at 1283 cm⁻¹ as two quanta of the CH₂ torsional motion, $2\nu_{21}$. The peak at 3647 cm⁻¹ is assigned as the OH stretch (ν_1), which has a literature value around 3650 cm⁻¹ in a N₂ matrix.³⁰ As in Figure 5, the feature around 4150 cm⁻¹ (also indicated with an asterisk) arises from the second anti-Stokes line of the 266 nm light Raman shifted in H₂ (218 nm).

C. Electronic Structure Results. The ab initio calculations showed several electronic configurations contribute to the excited states accessed near 200 nm for allyl iodide and for both room temperature conformers of allyl alcohol. For the interpretation of our data we consider only electronic configurations with CIS expansion coefficients greater than 0.2.²⁶ The relevant electronic configurations are listed in Table 2 with the CI weighting coefficient. Our ab initio calculations on allyl iodide show the excited state accessed at 199.7 nm involves three electronic configurations with coefficients greater than 0.2. The dominant configurations, shown in Figure 2, are $\pi \rightarrow$ Rydberg(16) and $\pi_{C=C}/n_1 \rightarrow \sigma^*_{C-I}/\pi^*_{C=C}$. A smaller contribution comes from another $\pi \rightarrow$ Rydberg(20) electronic configuration (the number of the Rydberg MO in parentheses). Our ab initio calculations on allyl iodide show another excited state with a vertical energy of 6.75 eV and an oscillator strength of $f = 0.30$ (approximately half that of the excited state at 7.06 eV). Considering the proximity of these two excited states and the relative oscillator strength of the two, the 6.75 eV state is most likely the shoulder just red of the 200 nm feature in the absorption spectrum of Boschi and Salahub.⁸ This excited state also has contributions from three electronic configurations: a mixed $\pi_{C=C}/n_1 \rightarrow \sigma^*_{C-I}/\pi^*_{C=C}$ configuration, a $\pi \rightarrow$ Rydberg(16) configuration, and a second $\pi \rightarrow$ Rydberg(20) configuration. We relate the similar electronic character of the 6.75 eV state and the 7.06 eV state to the features in common between our emission spectrum excited 199.7 nm and the allyl iodide emission spectra excited between 225 and 240 nm^{5,6} in section V.

As mentioned in section III, allyl alcohol has two dominant conformers at room temperature. The vertical excitation energy differs slightly between the two conformers, for the (sp,sc) conformer the excited state lies 7.57 eV above the ground state while for the (ac,-sc) conformer the excited state lies 7.71 eV above the ground state. Figure 3 shows the electronic configurations which contribute to the excited state of (sp,sc) conformer (Figure 1 bottom). The dominant configuration appears at the top of Figure 3 and is $\pi_{C=C}\pi^*_{C=C}$ in character. The other electronic configuration with a smaller CI coefficient has $\pi \rightarrow$ Rydberg(20) character. For the (ac,-sc) conformer of allyl alcohol (Figure 1, middle), the Franck-Condon region of the excited state has contributions from three principal electronic configurations. The largest contribution comes from a $\pi_{C=C}\pi^*_{C=C}$ electronic configuration. Two configurations with almost equal weighting in the CI expansion are from another $\pi_{C=C}\pi^*_{C=C}$ configuration and a $\pi_{C=C} \rightarrow$ Rydberg(20) configuration. We show these three configurations in Figure 4 ranked by CI coefficient.

V. Discussion

First, we discuss the emission spectrum of allyl iodide excited at 199.7 nm. As we stated previously, the two most intense peaks are ν_6 (C=C stretch) and ν_{10} (CH₂ wag). The most intense peak in the emission spectrum of allyl chloride at 199 nm was ν_6 (C=C stretch). This was taken as evidence of an excited state with $\pi\pi^*$ electronic character, in allyl chloride.¹⁶ Our ab initio calculations do not show any pure $\pi\pi^*$ character for the excited state near 200 nm in allyl iodide. However, the dominant three electronic configurations all involve the promotion of a π electron. Promotion of a π electron to a Rydberg orbital (Figure 2 top and bottom) leads to a decrease in the C=C bond character and thus an increase in the C=C bond length. A scan of the Franck–Condon region of the bright state using Gaussian 98²⁰ shows a sloped potential leading to longer C=C bond length. This is consistent with the observation of C=C stretch as both a fundamental and combination band.

The observation of ν_{10} as a fundamental, overtone, and in combination with ν_{20} (skeletal bending) indicates the methylene hydrogens bend out of the C=C–C plane in the excited state. As we noted previously, our ab initio calculations show significant contribution from electronic configurations involving the promotion of a π electron. The promotion of an electron from a π orbital on the C=C bond accounts for the stronger wagging motion observed in our spectrum, as the potential along the wag coordinate will be softer in the excited state.

We now consider whether the experimental emission spectrum of allyl iodide confirms the contribution to the excited-state character from a $\pi_{C=C}/n_I \rightarrow \sigma^*_{C-I}/\pi^*_{C=C}$ configuration as indicated in the low level electronic structure calculations. We might expect C=C torsional motion from a $\pi\pi^*$ configuration (as observed near 200 nm in allyl chloride¹⁶) or C–I stretch activity from $n_I\sigma^*_{C-I}$ (or $\pi\sigma^*_{C-I}$) character, but neither is observed in the emission spectrum. However, for allyl chloride, where the dominant gauche conformer is shown by ab initio electronic structure calculations to have considerable $n\sigma^*_{C-Cl}$ character in the Franck–Condon region, the emission spectrum shows only a weak feature in the C–Cl stretch.¹⁶ By analogy, activity in the C–I stretch in our allyl iodide emission spectrum might be obscured by the background from residual I₂. We can only conclude that the appearance of one of the strong features in the emission spectrum, the C=C stretch, and the absences of activity in torsion is more consistent with a dominant electronic contribution from a $\pi \rightarrow$ Rydberg(16) configuration, where one expects a lengthening of the C=C bond in the excited state with no significant force driving the molecules along the C=C torsional coordinate.

We now analyze the emission spectrum of Getty et al. at 224.63 nm⁵ and 237.11, 237.26, and 240.51 nm⁶ in light of our ab initio calculations. Their 224.63 nm spectrum⁵ is on resonance with a shoulder to the red of the 200 nm peak in the absorption spectrum of Boschi and Salahub.⁸ As discussed in section IVC, our ab initio studies show a state roughly 0.25 eV below the bright state with an oscillator strength approximately half that of the bright state. The electronic character of this lower energy state is qualitatively similar to the bright state. Getty et al. observed activity in ν_6 (C=C stretch) in their 224.63 nm spectrum; however, no torsional motion was observed.⁵ According to our ab initio calculations, the excited state they accessed has strong $\pi \rightarrow$ Rydberg(16) character leading to extended C=C bond lengths with little gradient along the torsional coordinate. As discussed previously, the observation of ν_{10} (CH₂ wag) is consistent with the softer potential in the wag coordinate of the excited state. Several low-energy motions

are also present in the spectrum at 224.63 nm. These are skeletal bending (ν_{19} and ν_{20}) and out-of-plane bending of the vinyl hydrogen (ν_{18}). These motions indicate the carbon skeleton is deforming significantly in the excited electronic state, possibly due to simple steric repulsion of the no longer doubly bonded structure. The spectra near 237 and 240 nm⁶ are quite similar to that at 224.63 nm. Though these wavelengths are well red of the shoulder, they are still on resonance with the same excited state accessed at 224.63 nm. Finally, the emission spectrum from excitation on resonance with the shoulder shows⁵ no strong features involving C–I stretch (a small feature near 670 cm⁻¹ may be C–I stretch). The lack of strong features involving the C–I stretch is consistent with our conclusions that the earliest structural changes in the excited state are not sensitive to the $\pi_{C=C}/n_I \rightarrow \sigma^*_{C-I}/\pi^*_{C=C}$ electronic configuration.

The emission spectrum of allyl alcohol is much simpler to interpret. First, the most intense feature in the spectrum (Figure 6) corresponds to C=C stretch with the first overtone of the C=C stretch present as well. Figures 3 and 4 show the electronic configurations involved in the excitation. The excited state of both conformers (sp,sc) and (ac,–sc) involves a $\pi\pi^*$ excitation. This contributes strong forces driving the molecule toward longer C=C bond lengths, giving the observed emission into C=C stretch. Moreover, we observed two quanta of the CH₂ torsion. A single quantum of torsion is not observed even though it is allowed by symmetry. However, the feature corresponding to one quantum of the torsion could be obscured by the broadened laser line (discussed in the section IVB). The $\pi\pi^*$ nature of the excited state provides considerable force along the torsional coordinate and we would expect the minimum along the torsional coordinate to lie somewhere away from a planar C=C conformation.

VI. Conclusions

We have collected the emission spectrum of allyl iodide and allyl alcohol under flow cell conditions with 199.7 nm excitation giving insight into the character of the Franck–Condon region of the excited state. Our emission spectrum of allyl iodide is qualitatively similar to that observed by Getty et al on resonance with the shoulder near 225 nm.^{5,6} Our ab initio electronic structure calculations suggest the excited states accessed near 200 nm and in the spectra of Getty et al. involve the promotion of a π electron to two Rydberg orbitals on the methylene carbon and an electronic configuration with $\pi_{C=C}/n_I \rightarrow \sigma^*_{C-I}/\pi^*_{C=C}$ character. However, the initial nuclear dynamics in the excited state, as evidenced by the emission spectrum, does not clearly substantiate the contribution from a $\pi_{C=C}/n_I \rightarrow \sigma^*_{C-I}/\pi^*_{C=C}$ configuration indicated by the ab initio electronic structure calculations. The emission spectrum of allyl alcohol excited at 199.7 nm shows the most intense activity in C=C stretch with some torsional motion. This is consistent with the ab initio calculations for this excited state which show significant contribution from $\pi\pi^*$ electronic configurations. Thus in both molecules the experimental emission spectra suggest that C–I fission in allyl iodide and production of the allyl radical from photolysis of allyl alcohol³¹ proceed via an electronic curve crossing or predissociation mechanism, not from excitation to an excited state with significant $n\sigma^*$ character in the Franck–Condon region.

Acknowledgment. This work was supported by the NSF under grant no. CHE 9619376. B.F.P. acknowledges the assistance of M. Shim in obtaining the absorption spectrum of allyl alcohol.

References and Notes

- (1) Imre, D.; Kinsey, J. L.; Sinha, A.; and Krenos, J. *J. Phys. Chem.* **1984**, *88*, 3956.
- (2) Johnson, B. R.; Kittrell, C.; Kelly, P. B.; Kinsey, J. L. *J. Phys. Chem.* **1996**, *100*, 7743.
- (3) Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822.
- (4) Jenkin, M. E.; Murrells, T. P.; Shalliker, S. J.; Hayman, G. D. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 433.
- (5) Getty, J. D.; Burmeister, M. J.; Westre, S. G.; Kelly, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 801.
- (6) Getty, J. D.; Liu, X.; Kelly, P. B. *J. Phys. Chem.* **1992**, *96*, 10155.
- (7) Arnold, P.; Cosofret, B.; Dylewski, S.; Houston, P.; Carpenter, B., manuscript in preparation.
- (8) Boschi, R. A.; Salahub, D. R. *Mol. Phys.* **1972**, *24*, 735.
- (9) Worrell, C. W. *J. Electron. Spectra* **1974**, *3*, 359.
- (10) Barnes A. J.; Holroyd, S. *Spectrochim. Acta* **1983**, *39A*, 579.
- (11) Camaggi, C. M.; Leardini, R.; Zanirato, P. *J. Org. Chem.* **1977**, *42*, 1570.
- (12) Baklanov, A. V.; Maltsev, V. P.; Karlsson, L.; Sassenberg, U.; Persson, A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1681.
- (13) Baklanov, A. V.; Maltsev, V. P.; Karlsson, L.; Lindgren, B.; Sassenberg, U. *Chem. Phys.* **1994**, *184*, 357.
- (14) Baklanov, A. V.; Aldener, M.; Lindgren, B.; Sassenberg, U. *J. Chem. Phys.* **2000**, *112*, 6649.
- (15) Shimo, N.; Nakashima, N.; Ikeda, N.; Yoshihara, K. *J. Photochem.* **1986**, *33*, 279.
- (16) Browning, P. W.; Kitchen, D. C.; Arendt, M. F.; Butler, L. J. *J. Phys. Chem.* **1996**, *100*, 7765.
- (17) Parsons, B. F.; Mueller, J. A.; Curry, S. L.; Ray, P. C.; Butler, L. *J. J. Chem. Phys.* **1999**, *111*, 8486.
- (18) Durig, J. R.; Tang, Q.; Little, T. S. *J. Raman Spectrosc.* **1992**, *23*, 653.
- (19) Vanhouteghem, F.; Pyckhout, W.; Van Alsenoy, C.; Van den Enden, L.; Geisse, H. J. *J. Mol. Struct.* **1986**, *140*, 33.
- (20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (21) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
- (22) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; von Ragué Schleyer, P. *J. Comput. Chem.* **1983**, *4*, 294.
- (23) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
- (24) Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 1878.
- (25) Hagen, K.; Shen, Q.; Stølevik, R. *J. Phys. Chem.* **1991**, *95*, 8632.
- (26) To convert the CI weighting coefficient output by Gaussian 98 for a singlet system into the percent character each electronic configuration contributes to the excited state, the coefficient must be squared and multiplied by two (accounting for both electron spin states).
- (27) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123.
- (28) McLachlan, R. D.; Nyquist, R. A. *Spectrochim. Acta* **1968**, *24A*, 103.
- (29) Rousseau, D. L.; Williams, P. F. *J. Chem. Phys.* **1976**, *64*, 3519.
- (30) Silvi, B.; Perchard, J. P. *Spectrochim. Acta* **1976**, *32A*, 11.
- (31) Szpunar, D. E.; Morton, M. L.; Butler, L. J., private communication of work in progress.