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Single-photon and resonance-enhanced multiphoton threshold ionization of the allyl radical

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Pulsed-field-ionization zero-kinetic-energy photoelectron spectra of jet-cooled allyl radical (C3H5) have been recorded following single-photon and resonant multiphoton excitation. Simulations based on an orbital ionization model and rovibronic photoionization selection rules reliably describe the observed intensity distributions in the photoelectron spectra obtained from single-photon excitation from the ground state and resonant multiphoton excitation via the 3s and the 3p Rydberg states. More than 30 transitions to vibrational levels of the cation were identified and assigned on the basis of predictions from ab initio calculations. © 2009 American Institute of Physics.

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I. INTRODUCTION

The allyl radical is the simplest organic molecule with a conjugated π-electron system. The electronic spectrum of allyl has been studied extensively and the structural and dynamic properties of many vibronically excited states of allyl have been characterized by optical spectroscopy.1–6 The ground electronic state of allyl has also been investigated by electron spin resonance (ESR) spectroscopy.7,8 From these ESR studies and theoretical investigations,9 the spin density on the terminal carbon atoms was determined to have a gerade-π-type orbital character.

The allyl radical plays an important role in combustion10 and interstellar chemistry,11 and its adiabatic ionization energy represents an important quantity in the evaluation of thermochemical reaction cycles. The first photoelectron spectrum of the allyl radical12 enabled the determination of the adiabatic ionization energy as 8.13 ± 0.02 eV. Slightly higher values, ranging up to 8.15 eV, were reported in later works.13–16 The most recent measurements of the adiabatic ionization energy of allyl carried out by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy using multiphoton14 and single-photon excitation schemes17,18 yielded values differing by as much as 0.22 meV. These measurements provided important information on the vibrational energy level structure of C3H5+. In Ref. 17, the photoelectron associated with the formation of the X+ → A1 state of C3H5+ was assumed to have a gerade-ℓ orbital angular momentum quantum number, an assumption that appears to contradict the “chemical” intuition that photoemission from a d-type orbital (see Fig. 1) should result in ungerade-ℓ photoelectron partial waves.

To resolve these ambiguities in the interpretation of the photoelectron spectrum of allyl, the PFI-ZEKE photoelectron spectra of allyl obtained following single-photon and resonant multiphoton excitation via several selected vibrational levels of the B and C intermediate states were measured to access a wider range of vibrational levels of the allyl cation.19 We present here the results of this investigation and the analysis of the rotational contours observed in both the single-photon- and the multiphoton photoelectron spectra recorded via the B and C intermediate levels based on an orbital ionization model20 and MR-CISD ab initio calculations.21 This model enabled us to confirm the symmetry assignment21 of the intermediate electronic states.

II. EXPERIMENTAL

A. The single-photon PFI-ZEKE photoelectron spectra

The threshold photoionization of C3H5 was studied from the ground neutral state by single-photon photoionization and PFI-ZEKE photoelectron spectroscopy. The experimental setup has been described in Refs. 22 and 23 and only aspects specific to these measurements on allyl are summarized here. The allyl radicals were produced photolytically from 1,5-hexadiene (Aldrich, 97%). The carrier gas argon was bubbled through a sample of the 1,5-hexadiene precursor at room temperature. Photolysis by the 193 nm output of an ArF excimer laser (LambdaPhysik, Compex) was achieved in a quartz capillary mounted at the end of a pulsed nozzle allowing for the cooling of the allyl radicals in a supersonic expansion from the capillary into vacuum (see Ref. 24). Rotational temperatures ranging from 20 to 50 K were obtained in this way, depending on the nozzle stagnation pressure and the position of the focus of the 193 nm photolysis laser beam along the capillary axis, as determined from the rotational contours of the bands observed in the PFI-ZEKE photoelectron spectra. Tunable vacuum-ultraviolet (VUV) radiation in the region of the adiabatic ionization threshold was generated by resonance-enhanced difference-frequency mixing (νVUV=2ν1−ν2) in a cell.
thereon, the HOMO, SOMO, and LUMO are valence orbitals. A

\[ \text{HOMO}_{p_z}, \text{SOMO}_{d_z}, \text{LUMO}_{3p_x} \]

FIG. 1. MO diagram relevant for the description of the five lowest-lying states of neutral allyl and the ground state of C\(_3\)H\(_5\). The configurations on the right-hand side are labeled in the C\(_3\)H\(_5\)(M) molecular symmetry group and, in each case, the CI coefficient of the dominant contribution to the electronic wave function is indicated as obtained in Ref. 21. Each orbital is given a symmetry label reflecting its dominant \( \ell \sigma \) single-center expansion contribution, where \( \ell \sigma \) and \( \lambda' \) represent the quantum numbers associated with the orbital angular momentum and its projection onto the z-axis of the molecule-fixed axis system. The 3s, 3p\(_x\), 3p\(_y\), and 3p\(_z\) orbitals are Rydberg orbitals, whereas the HOMO, SOMO, and LUMO are valence orbitals. A schematic representation of allyl and the definition of the principal and inertial axis systems are given at the bottom left.

filled with krypton using the \((4p)^5(3p_2)5p[1/2](J=0) \leftrightarrow (4p)^61S_0\) two-photon resonance in krypton at \(2\nu_1 = 94 092.862 \text{ cm}^{-1}\) as described in Ref. 25.

Photoionization spectra were measured by recording the C\(_3\)H\(_5^+\) ion signal mass selectively as a function of the VUV wave number \(\nu_{\text{VUV}}\). The C\(_3\)H\(_5^+\) ions were extracted by applying a 2 kV pulsed voltage to the extraction plates of 2 \(\mu\)s after photoexcitation and detected on the microchannel-plate (MCP) detector.

PFI-ZEKE photoelectron spectra were recorded as a function of the VUV wave number by monitoring the electrons produced by PFI of high-\(n\) Rydberg states. A “discrimination” pulse of 1 \(\mu\)s duration and +88 mV/cm amplitude was applied at 2.5 \(\mu\)s after photoexcitation to field ionize the highest Rydberg states and sweep free electrons out of the photoexcitation region. This discrimination pulse was immediately followed either by a single “detection” pulse of –526 mV/cm or three successive detection pulses of –140, –263, and –877 mV/cm each of 500 ns duration. These detection pulses field ionized the high-\(n\) Rydberg states and accelerated the electrons toward the MCP detector.

The photoionization and PFI-ZEKE photoelectron spectra were calibrated by recording with each scan an optogalvanic spectrum of Ne. To determine the position of the field-free adiabatic ionization threshold, corrections of 1.3(2), 1.6(2), 2.3(4), and 1.8(2) \(\text{cm}^{-1}\) for detection pulses of –140, –263, –877, and –526 mV/cm, respectively, were introduced to compensate for the shifts in the ionization thresholds induced by the electric-field pulse sequence according to the procedure described in Ref. 26.

B. Resonant multiphoton ionization experiments

The experimental apparatus is a modified version of the one described previously\(^26\)\(^27\) and we give only a brief description here. We generated a clean pulse of allyl radicals by supersonic jet flash pyrolysis\(^28\) of 1,5-hexadiene seeded in 1.5 bar of helium. The second harmonic output of an Nd:yttrium aluminum garnet (YAG)-pumped dye laser provided ultraviolet or visible light needed for recording the 1+1 and 2+2 resonance-enhanced multiphoton ionization (REMPI) spectra of the allyl radical. For the 1+1’ and 2+1’ resonant multiphoton PFI-ZEKE experiments, a second Nd:YAG-pumped dye laser provided visible light to excite the vibronically excited allyl radicals to high-\(n\) Rydberg states. We used neon and argon optogalvanic hollow cathode lamps for wavelength calibration of the two dye lasers. The collimated counterpropagating laser beams crossed the skinned radical beam inside the source of a linear time-of-flight mass spectrometer. The ions were detected using double MCPs. In the PFI-ZEKE photoelectron spectroscopic experiments, a single pulse of –12 V/cm applied after a field-free delay time of 0.9 \(\mu\)s was used to extract the PFI-ZEKE photoelectrons into a 75 mm long field-free drift tube at the end of which they were detected on double MCPs. We applied a correction of 5.8 cm\(^{-1}\) to obtain the field-free ionization thresholds.\(^26\)

For the 2+1’ excitation, a 300 mm lens was used to focus the 4.5 ml/pulse fundamental output of the dye laser into the photoexcitation region. The high intensity needed for two-photon electronic excitation led to an ac Stark shift of 9.9 cm\(^{-1}\) which we determined by extrapolation of the band positions measured at pulse energies of 4.5, 2.5, 1.5, and 0.75 mJ and corrected for. In a separate 2+1’ REMPI experiment, we found that the lower intensity of the 1’ ionization laser pulse made a negligible contribution to the magnitude of the ac Stark shift.

III. ROVIBRONIC PHOTIONIZATION SELECTION RULES AND IONIZATION DYNAMICS

Allyl is represented schematically at the bottom of Fig. 1 where its molecule- and laboratory-fixed axis systems used for the labeling of the molecular orbitals (MOs) are also presented. The geometries and orbitals of the five lowest-lying electronic states have been computed at the MR-CISD level of theory.\(^21\) The \(\tilde{B}\) and \(\tilde{E}\) states were found to be separated by \(\approx 0.7 \text{ eV}\) in energy and to be of 3s and 3p\(_y\) Rydberg orbital character, respectively. Two further Rydberg states corresponding to 3p\(_x\) and 3p\(_y\) orbitals have been identified at energies between those of the 3s and 3p\(_x\) Rydberg states.\(^21\) The energetic ordering of the 3p states, however, could not be established unambiguously from these calculations. The 3p\(_x\) and 3p\(_y\) orbitals lie in the plane of the molecule and are almost degenerate. The MOs which are singly occupied in the main configurations contributing to the five lowest-lying
TABLE I. Rovibronic symmetry selection rules for transitions from vibronic states of C3H5, of symmetry Γc, to the cationic vibronic ground state $\tilde{X}^+$ $^1A_1(0^0)$ in dependence of the angular momentum of the ejected photoelectron $\ell$. The last column lists the states of neutral allyl of the corresponding electronic symmetry (i.e., $\Gamma_c^e=\Gamma_{c_0}^e$).

<table>
<thead>
<tr>
<th>$\Gamma_{re}$</th>
<th>$\ell$</th>
<th>$\Delta K_a$</th>
<th>$\Delta K_c$</th>
<th>Initial state</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Even</td>
<td>Odd</td>
<td>Odd</td>
<td>$\tilde{B}$ and $\tilde{D}$</td>
</tr>
<tr>
<td>A2</td>
<td>Even</td>
<td>Even</td>
<td>Even</td>
<td>$\tilde{X}$</td>
</tr>
<tr>
<td>B1</td>
<td>Odd</td>
<td>Odd</td>
<td>Odd</td>
<td>$\tilde{A}$ and $\tilde{E}$</td>
</tr>
<tr>
<td>B2</td>
<td>Even</td>
<td>Even</td>
<td>Odd</td>
<td>$\tilde{C}$</td>
</tr>
</tbody>
</table>

Electronic states from these ab initio calculations are displayed on the left hand side of Fig. 1. Except for the $\tilde{A}^2B_1$ state, which is strongly mixed, most states can be represented by a dominant configuration, the square of the configuration interaction (CI) coefficients being at least 0.8. The $\tilde{X}^2B_1$ state has 80% 3$p_z$ character and is mixed mainly with the lowest unoccupied molecular orbital (LUMO) of $B_1$ symmetry.

The qualitative structure of the highest occupied molecular orbital (HOMO), the singly occupied molecular orbital (SOMO), and the LUMO relevant to the present study is also displayed in Fig. 1. The symmetry labels are given below each electronic state in Fig. 1. The MO associated with the unpaired electron in the neutral ground state has electron density at the terminal carbons and no density at the central carbon, in agreement with the results of the ESR studies mentioned above.7,8

The photionization selection rules and the orbital ionization model used in the simulations of the rotational intensity distribution are discussed in more details in Refs. 20, 29, and 30. When applied to allyl [molecular symmetry group $C_{2v}(M)$] (Ref. 31) the general rovibronic photoionization selection rules given by

$$\Gamma_{re}^\nu \otimes \Gamma_{re}^+ \supseteq (A_2)^{(\ell+1)},$$  

(1)

where $\ell$ represents the orbital angular momentum quantum number of the outgoing photoelectron partial wave and $\Gamma_{re}^+$ and $\Gamma_{re}^\nu$ represent the rovibronic symmetry of C3H5 and C3H5, respectively. For the photoionization transitions to the $\tilde{X}^+ \,^1A_1$ vibronic ground state of C3H5, the selection rules can be expressed in terms of changes in the usual asymmetric-top angular momentum projection quantum numbers $K_a$ and $K_c$. Table I summarizes these selection rules for ionization out of states of $A_1$, $A_2$, $B_1$, and $B_2$ vibronic symmetries. The electronic state that possesses the corresponding vibronic symmetry in its vibrational ground state is indicated in the fifth column of Table I.

Conservation of the total angular momentum excluding spin can be expressed in the electric dipole approximation by the selection rule

$$\Delta N = N^+ - N^0 = \ell + 1, \ell, \ldots, -\ell, -\ell - 1,$$  

(2)

where $N^0(N^+)$ is the total angular momentum excluding spin of the neutral (cationic) molecule.

To model the rovibrational intensity distributions we used Eq. (7) from Ref. 20, which was derived within a simple orbital ionization model. From this model the propensity rule $|\Delta K_a| + |\Delta K_c| = |\ell'|$ for a II’-type near-prolate top is obtained, where $\ell'$ represents the quantum number associated with the projection on the principal axis of the angular momentum of the orbital out of which ionization occurs. These propensity rules are more restrictive than those implied by the symmetry selection rules in Eq. (1).

The SOMO out of which ionization occurs in the $\tilde{X}^+ \,^1A_1 \leftrightarrow \tilde{X}^2A_2$ transition of allyl is depicted in Fig. 1 and is of $A_2$ symmetry in the $C_{2v}(M)$ molecular symmetry group. A MO of $A_2$ symmetry is antisymmetric with respect to the inversion operation $E^+$ and the inversion permutation of the terminal CH2 entities, which are isomorphic to reflections in the xy- and xz-plane symmetry planes of the $C_{2v}$ point group. Both of these symmetry planes must correspond to nodal planes of a MO of $A_2$ symmetry of the $C_{2v}$ point group. Therefore, the MO out of which ionization occurs has two nodal planes containing the symmetry or quantization axis [i.e., the z(b)-axis along the central C=H bond in Fig. 1]. Only MO components with $\lambda'' = \pm 2$ (represented by the subscript $\delta$) of $A_2$ symmetry, and therefore only $d_\delta$ and $f_\delta$ are expected to contribute significantly to the single-center expansion of the SOMO of $A_2$ symmetry.

The authors of Ref. 17 state that the $\tilde{X}^+ \,^1A_1 \leftrightarrow \tilde{X}^2A_2$ photoionizing transition primarily results in the emission of photoelectron partial waves with gerade values of the total angular momentum quantum number $\ell$, because in their opinion, the MO out of which ionization occurs is a 2$p_z$ atomiclike orbital (the subscript $\pi$ corresponds to $\lambda'' = \pm 1$). Consideration of the SOMO in Fig. 1, however, leads to the conclusion that this orbital has dominant $d_\delta$ character and that therefore ungerade-$\ell$ photoelectron partial wave components are important. Different $\Delta K_a$ and $\Delta K_c$ selection rules are obtained depending on whether ionization occurs out of a $p_{\pi}$, see Eq. (3),33 as assumed in Ref. 17, or $d_\delta$ MO, see Eq. (4),

$$\Delta K_a = \text{even}, \Delta K_c = \text{even} \quad \text{for} \quad \Gamma_{ve} = A_2, \ell = \text{even},$$  

(3)

$$\Delta K_a = \text{odd}, \Delta K_c = \text{odd} \quad \text{for} \quad \Gamma_{ve} = A_2, \ell = \text{odd}.$$  

(4)

To facilitate the assignment of the congested spectra of the intermediate states, predictions of the rotational contours of the PFI-ZEKE photoelectron spectra recorded through the $3s, 3p_\pi, 3p_\sigma$, and $3p_\delta$ intermediate states have been made on the basis of Eq. (7) of Ref. 20. Figures 2(a)–2(d) show predictions of the rotational contours of transitions from selected intermediate levels to the cationic vibronic ground state ($\tilde{X}^+ \,^1A_1$). Because of their Rydberg character the $3s$, $3p_\pi$, $3p_\sigma$, and $3p_\delta$ orbitals consist of only one dominant contribution in the single-center expansion, i.e., $s_\delta(A_1)$, $p_\delta(A_1)$, $p_{\pi}(B_1)$, and $p_{\delta}(B_2)$, respectively. Depending on the vibronic symmetry of the intermediate state, different $\Delta K_a$ and $\Delta K_c$ selection rules are obtained as summarized in Table I. More-
corresponding to the experimental resolution. Whereas the scheme led to the selective excitation of rotational levels states of the intermediate level at a rotational temperature of 35 K is displayed on the bottom trace and has been shifted along the vertical axis for clarity.

FIG. 3. (a) Photoionization (top trace) and PFI-ZEKE photoelectron (middle trace) spectra of allyl in the region of the first adiabatic ionization threshold. A simulation of the spectrum based on the orbital ionization model and assuming a rotational temperature of 25 K is displayed on the bottom trace and has been shifted along the vertical axis for clarity. (b) Upper trace: PFI-ZEKE photoelectron spectrum of the $\tilde{X}^1 \Sigma^+_g(1^1 \Sigma^-_g) \rightarrow \tilde{X}^1 \Sigma^+_g(0^0 \Sigma^-_g)$ transition of allyl. Bottom trace: The simulation based on the orbital ionization model and assuming a rotational temperature of 35 K. The simulated spectrum has been shifted along the vertical axis for clarity.

spectra displayed in Figs. 2(a) and 2(b) are very similar because the MOs out of which ionization occurs are of the same symmetry and have the same value of $\lambda'$, the spectra shown in Figs. 2(c) and 2(d) have distinctly different band shapes. The different band shapes predicted for the PFI-ZEKE photoelectron spectra could thus be used to assign the intermediate levels.

IV. RESULTS

A. The one-photon PFI-ZEKE photoelectron spectra

The PFI-ZEKE photoelectron spectra of allyl in the vicinity of the $\tilde{X}^1 \Sigma^+_g(00 \Sigma^-_g)$ and the $\tilde{X}^1 \Sigma^+_g(71 \Sigma^-_g) \rightarrow \tilde{X}^1 \Sigma^+_g(00 \Sigma^-_g)$ transitions are displayed in Figs. 3(a) and 3(b), respectively. The photoionization spectrum of allyl [top trace in Fig. 3(a)] exhibits a sharp rise from zero at the position of the lowest band of the PFI-ZEKE photoelectron spectrum which indicates that (1) the PFI-ZEKE photoelectron signal indeed originates from the allyl radical and (2) the contribution from hot bands is not significant. Because of the absence of sharp resonances in the photoionization spectrum which results, at least in part, from spectral congestion, the intensity distribution observed in the photoelectron spectrum is not expected to be strongly perturbed by the effects of channel interactions, which often complicate the interpretation of PFI-ZEKE photoelectron spectra. The PFI-ZEKE photoelectron spectra of both bands are congested with little rotational structure resolved apart from a reproducible double-peak structure close to the band center with a separation of about 9 cm$^{-1}$. The FWHM of the bands amounts to $\approx 40$ cm$^{-1}$. The bottom traces in Figs. 3(a) and 3(b) are simulations of the PFI-ZEKE photoelectron spectra based on the orbital ionization model (see Sec. III and Ref. 20) and

over, for different values of the quantum number $\lambda'$ (a single prime indicates the intermediate state) of the projection of the orbital angular momentum onto the figure axis, different propensity rules for $\Delta K_a$ and $\Delta K_c$ are obtained. In the simulations, a thermal distribution of the population of rotational states of the intermediate level at a rotational temperature of 150 K was assumed. Because the first step in the excitation scheme led to the selective excitation of rotational temperature with $K_a = 5$, only transitions from the intermediate state with $K_a = 5$ to the cationic ground state were taken into account. The spectra were convoluted with a Gaussian instrumental function of full width at half maximum (FWHM) of 3 cm$^{-1}$, corresponding to the experimental resolution. Whereas the
rotational temperatures of 25 K [Fig. 3(a)] and 35 K [Fig. 3(b)]. No attempt to fit the rotational constants of the neutral or the cationic ground state of allyl was undertaken. The simulations were performed using the constants summarized in Table II.\textsuperscript{2,17,35} The adiabatic ionization energy $E_i$ was determined to be 65 580.1(20) \textsuperscript{a} \text{cm}^{-1} \text{[8.130 88(24) eV]}. This result thus confirms the value of the first adiabatic ionization energy (65 584.6(20) \text{cm}^{-1}) determined by Xing \textit{et al.}\textsuperscript{17} The fundamental wave number of the C–C–C bending mode $v_C^B$ of the cation was determined to be 434.5(10) \text{cm}^{-1} (see also Table IV).

The simulations shown on the bottom traces of Figs. 3(a) and 3(b) reproduce the contours of the experimental spectra well but underestimate the contrast of the central double peak structure. In the simulations, the $d_\delta$ and $f_\delta$ components of the SOMO of allyl have been weighted in a ratio of 2:1, respectively. The analysis of the PFI-ZEKE photoelectron spectrum based on the qualitative structure of the SOMO shown in Fig. 1 thus supports the conclusion drawn from ESR spectra that the spin density is localized at the terminal carbon atoms.\textsuperscript{7,8}

### Table II. First adiabatic ionization energy $E_i$, rigid-rotor asymmetric-top rotational constants, and fundamental wave number of the C–C–C bending ($v_C^B$) mode of C$_3$H$_5$ and C$_3$H$_5^+$ used in the simulations of the experimental spectra. Selected values of the $v_C^B$ and $E_i$ from the literature are given for comparison.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^\prime$ cm$^{-1}$</td>
<td>1.801 597$^a$</td>
</tr>
<tr>
<td>$B^\prime$ cm$^{-1}$</td>
<td>0.346 339 $^a$</td>
</tr>
<tr>
<td>$C^\prime$ cm$^{-1}$</td>
<td>0.290 232 $^a$</td>
</tr>
<tr>
<td>$A^\prime$ cm$^{-1}$</td>
<td>1.618 $^b$</td>
</tr>
<tr>
<td>$B^\prime$ cm$^{-1}$</td>
<td>0.351 $^b$</td>
</tr>
<tr>
<td>$C^\prime$ cm$^{-1}$</td>
<td>0.288 $^b$</td>
</tr>
<tr>
<td>$A^\prime$ cm$^{-1}$</td>
<td>1.643 $^3$</td>
</tr>
<tr>
<td>$B^\prime$ cm$^{-1}$</td>
<td>0.3686 $^c$</td>
</tr>
<tr>
<td>$C^\prime$ cm$^{-1}$</td>
<td>0.3010 $^c$</td>
</tr>
<tr>
<td>$A^\prime$ cm$^{-1}$</td>
<td>1.6729 $^d$</td>
</tr>
<tr>
<td>$B^\prime$ cm$^{-1}$</td>
<td>0.3689 $^d$</td>
</tr>
<tr>
<td>$C^\prime$ cm$^{-1}$</td>
<td>0.3009 $^d$</td>
</tr>
</tbody>
</table>

$E_i/(hc \text{ cm}^{-1})$

- 65 580.1(20)$^e$
- 65 584.6(20)$^f$
- 65 762$^{21,21}$
- 65 573(81)$^{21,21}$

$^a$Reference 35.
$^b$Reference 2.
$^c$Reference 17.
$^d$This work, corrected for the field-induced shift.
$^e$Reference 14.
$^f$Reference 18.

B. The resonance-enhanced multiphoton ionization spectra

Figure 4 shows an overview of the 1+1 (lower trace) and the 2+2 (upper trace) REMPI spectra of the allyl radical in the energy range from 39 500 to 41 700 cm$^{-1}$. The prominent band centered at 40 042 cm$^{-1}$ in the 2+2 REMPI corresponds to the origin of the $\tilde{B}$ $^2A_1$ state, the 3s-Rydberg state forbidden in one-photon excitation. Strong vibronic coupling of the $\tilde{B}$-state to the 3p-Rydberg states results in a complicated and rich vibronic structure in the 1+1 REMPI spectrum in this energy range that was first analyzed by Blush \textit{et al.}\textsuperscript{1} We recently measured rovibrationally cold ($T_{\text{rot}} \sim 6$ K) REMPI spectra in the same energy range and used these together with the rovibrationally warm ($T_{\text{rot}} \sim 250$ K) REMPI spectra shown in Fig. 4 to identify a large number of hot bands that were previously assigned to vibrational levels of the $\tilde{B}$ $^2A_1$ and the $\tilde{E}$ $^2B_1$ electronic states. Together with electronic structure calculations of the electronically excited states and the analysis of the PFI-ZEKE photoelectron spectra in this report, we completely reassigned the vibronic bands that appear in Fig. 4. Our revised assignments [in the notation $i\nu^p$, where $i$ designates the vibrational mode with $\nu^p$ (\nu$^p$) quanta of excitation in the ground (intermediate) electronic state] for those bands appear in Table III and are discussed in Ref. 21.

C. The 1+1’ and 2+1’ PFI-ZEKE photoelectron spectra

The 1+1’ and the 2+1’ PFI-ZEKE photoelectron spectra obtained through the intermediate states listed in Table III are displayed in Fig. 5. The intermediate electronic states all have Rydberg character and the assignment of the corresponding transitions is indicated on the right-hand side of the figure. Excitation to the $\tilde{B}$ $^2A_1$ state corresponds to a $n \rightarrow 3s$ transition in a simple MO picture and excitation to the $\tilde{C}$ $^2B_2$ state to a $n \rightarrow 3p_s$ transition, see Fig. 1. Those Rydberg states have a geometry that is very similar to that of the cationic ground state, and from a simple Franck–Condon argument, we expect that $\Delta \nu=0$ transitions are particularly intense in the PFI-ZEKE photoelectron spectra.

The top trace in Fig. 5 shows the PFI-ZEKE photoelectron spectrum obtained following the excitation to the $\tilde{B}$ $^2A_1$ state origin with one intense peak that we assign as the cationic origin band. A second weaker peak is visible at $+433$ \text{cm}^{-1} that we assign to a transition to the $71^l$ vibrational level of the cation. The photoelectron spectrum recorded via the $\tilde{B}$ $12^0$ transition is very similar with only one peak with a FWHM$=4$ \text{cm}^{-1}. In contrast, the shape of the cationic origin
band observed by exciting the $\tilde{C} \, ^2B_2$ state origin is rather different, see also Fig. 2. The poor signal-to-noise ratio of this trace arises from the short excited state lifetime of only 12 ps for that state compared to the $\tilde{B}$ state origin that has a lifetime of 22 ps. From the average wave number of these three intense cationic origin bands we obtain a value of 65 581.3(80) cm$^{-1}$ for the first ionization energy of the allyl radical, in excellent agreement with the value obtained from the one-photon VUV PFI-ZEKE photoelectron spectrum (see Sec. IV A and Ref. 17).

We also measured PFI-ZEKE photoelectron spectra by excitation to a large number of vibrational levels of the $\tilde{B} \, ^2A_1$ state in the 39 500–41 700 cm$^{-1}$ wave number range. The positions of all observed vibrational levels of the cation with their assignments are listed in Table IV along with the anharmonic vibrational frequencies calculated $ab\,\text{initio}$ at the HCTH147/TZ2P level of theory. The vibration of the cation with the lowest wave number ($\nu_{12}^r = 283$ cm$^{-1}$) in the cation is the conrotatory twist of the terminal methylene groups that we observe in the 1+1’ PFI-ZEKE photoelectron spectra recorded from the $\tilde{B} \, 12^1$ and the $\tilde{B} \, 7^112^1$ states. In the $\tilde{B}$ state this vibration has a fundamental wave number of 254 cm$^{-1}$. We assign the band observed 583 cm$^{-1}$ above the origin in the 1+1’ PFI-ZEKE photoelectron spectra recorded through the $\tilde{B} \, 12^2$ and $\tilde{B} \, 7^112^2$ states to the 12$^2$ cationic state. From the fundamental as well as the first overtone of $\nu_{12}^r$, we determine the anharmonic constant $\chi_{12,12}(\tilde{B}) = +7.0$ cm$^{-1}$ (Ref. 21) as expected, because the potential energy surface of the 3s Rydberg state should strongly resemble that of the cationic ground state.

The second lowest frequency vibrational mode in the cation is the C–C–C bend $\nu_9^r$ with a fundamental wave number of 433 cm$^{-1}$ and a first overtone assigned to the band observed at 872 cm$^{-1}$ above the origin in the spectrum recorded from the $\tilde{B} \, 7^1$ intermediate state (see fifth and sixth traces from the top in Fig. 5). In many PFI-ZEKE photoelectron spectra shown in Fig. 5, we also observed weaker bands located at 433 cm$^{-1}$ above the fundamental bands and we assign these bands to the combination bands with the $\nu_9^r$ mode. The low intensity of this band can be rationalized by the slightly different C–C–C–bond angle of the 3s Rydberg state compared to that in the cationic ground state. We also attribute a band to the disrotatory twist of the terminal methylene groups ($\nu_8^r$, fundamental wave number of 603 cm$^{-1}$) in the PFI-ZEKE photoelectron spectrum recorded from the $\tilde{B} \, 9^1$ intermediate state. This wave number is only slightly

![Figure 5](https://publishing.aip.org/authors/rights-and-permissions)
TABLE IV. Experimental cation vibrational frequencies observed in the multiphoton PFI-ZEKE photoelectron spectra compared to anharmonic vibrational frequencies obtained at the HCTH147/TZ2P level of theory. The uncertainty in the experimental wave numbers is estimated to be ±2 cm⁻¹.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
<th>$v_{expt}$/cm⁻¹</th>
<th>$v_{calc}$/cm⁻¹</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>iph CH stretch</td>
<td>3103</td>
<td>3112/3113</td>
<td></td>
</tr>
<tr>
<td>$v_2$</td>
<td>CH$_2$ stretch</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$v_3$</td>
<td>CH stretch</td>
<td>3049</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_4$</td>
<td>CH$_2$ scisscors</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$v_5$</td>
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<td>1267b</td>
<td></td>
</tr>
<tr>
<td>$v_6$</td>
<td>CCC stretch</td>
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<td>1043b</td>
<td></td>
</tr>
<tr>
<td>$v_7$</td>
<td>CCC bend</td>
<td>433(2)</td>
<td>427</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>434.5(10)$^a$</td>
<td>436.3(20)$^d$</td>
<td></td>
</tr>
<tr>
<td>$v_8$</td>
<td>CH$_2$ oop bend</td>
<td>1116</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_9$</td>
<td>CH$_2$ twist</td>
<td>603(2)</td>
<td>571</td>
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<tr>
<td>$v_{10}$</td>
<td>CH oop bend</td>
<td>1009(2)</td>
<td>1011 $-1/025^a$</td>
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<tr>
<td>$v_{11}$</td>
<td>CH$_2$ oop bend</td>
<td>1111(2)</td>
<td>1111 1136/1130$^a$</td>
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<td>CH$_2$ twist</td>
<td>283(2)</td>
<td>304</td>
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<tr>
<td>$v_{13}$</td>
<td>CH$_2$ stretch</td>
<td>3100</td>
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<td></td>
</tr>
<tr>
<td>$v_{14}$</td>
<td>CH$_2$ stretch</td>
<td>2989</td>
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</tr>
<tr>
<td>$v_{15}$</td>
<td>CH$_2$ scisscors</td>
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<td>1578b</td>
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<td>$v_{16}$</td>
<td>CH bend</td>
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<td>1418b</td>
<td></td>
</tr>
<tr>
<td>$v_{17}$</td>
<td>CCC stretch</td>
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<td>1265 1249b</td>
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<tr>
<td>$v_{18}$</td>
<td>CH$_2$ rock</td>
<td>937</td>
<td>928b</td>
<td></td>
</tr>
</tbody>
</table>

Vibrational level

12$^2$ | 583(2) | 616 |
7$^112^1$ | 702(2) | 719 |
7$^2$ | 872(2) | 856 |
7$^112^2$ | 989(2) | 1022$^e$ |
7$^10$ | 1030(2) | 988 |
7$^112^1$ | 1130(2) | 1146$^f$ |
6$^112^1$ | 1315(2) | 1331 |
7$^2$ | 1410(2) | 1416$^f$ |
7$^10$ | 1439(2) | 1438 |
7$^1117^1$ | 1751(2) | 1694 |

$^a$Ar/N$_2$ tagged, see Ref. 36.
$^b$From Ref. 37.
$^c$From single-photon experiments.
$^d$From single-photon experiments in Ref. 17.
$^e$Value calculated by adding the wave numbers of the 7$^2$ and 12$^2$.
$^f$Value calculated by the wave numbers of the 7$^2$ and the 12$^2$.

The PFI-ZEKE photoelectron spectra recorded from the $\bar{B}$ 17$^1$ and the $\bar{B}$ 6$^112^1$ intermediate states reveal two strong and partially overlapping bands that arise because the rotational contours of the $\bar{B}$ 17$^1$ state and the $\bar{B}$ 6$^112^1$ state overlap in the REMPI spectra with band origins separated only by 4.0 cm⁻¹. The PFI-ZEKE photoelectron spectra obtained from those two states show two distinct peaks that we assign to the $v_{17}^*$ and the $v_{17}^*+v_{12}^*$ vibrations. Given the very small wave number differences between these levels, their assignment remains uncertain. The slight shift in frequency of those vibrational levels observed in the PFI-ZEKE photoelectron spectra arises from the different rotational states that are prepared in the intermediate states.

V. DISCUSSION AND CONCLUSIONS

The photoionization dynamics of allyl have been investigated in the region of the adiabatic ionization thresholds by photoionization and PFI-ZEKE photoelectron spectroscopy. The selection rules for the transitions $X^2\Pi(0,7^1) \rightarrow A_1 ^2\Pi \rightarrow \bar{X}(0^0) ^2A_2 ^2$ were derived and found to be different from those used in Ref. 17 because of different assumptions concerning the MO out of which ionization occurs. Simulations based on the orbital ionization model were performed, describing the SOMO of allyl as a single-center expansion with significant contributions from $d_s$ and $f_s$ angular momentum characteristics only in agreement with theoretical and ESR studies,7,9 but in disagreement with the analysis presented by Xing et al.17 The wave numbers of several vibrational levels of the allyl cation could be determined for the first time and generally agree well with the ab initio predictions made at the HCTH147/TZ2P level of theory. The largest discrepancy (32 cm⁻¹) is observed for the methylene group twisting mode ($v_{10}^*$). Both the $v_{10}^*$ CH bending and $v_{11}^*$ CH$_2$ bending modes were observed at lower frequencies in the infrared photodissociation spectrum of allyl cation tagged with rare gas atoms and N$_2$ molecules.36 However, the differences can be explained by the interaction of the allyl cation with the complex partner.

The intensity distributions and rotational contours of the bands of the PFI-ZEKE photoelectron spectra of allyl recorded via different vibrational levels of the $\bar{B}$ and $\bar{C}$ states vary strongly. Predictions of these intensity distributions and band contours made in the realm of the orbital ionization model suggest that the bands recorded through totally symmetric vibrational levels of the $\bar{B}^2\Pi_1$ or $\bar{D} ^2\Pi_1$ intermediate states should be sharp and dominated by a strong Q-type branch, and that the bands recorded through the $\bar{E} ^2B_1$ and $\bar{C} ^2B_2$ levels should be significantly broader as confirmed experimentally. These predictions may help in assigning spectra of the partially overlapping $3s, 3p_x, 3p_y$, and $3p_z$ Rydberg states of allyl.

ACKNOWLEDGMENTS

This work was supported financially by ETH Zurich and the Swiss National Science Foundation under Project Nos. 200020-116245 and 200020-115974.

The nomenclature used here to designate the electronically excited states and energetic ordering and symmetry assignments made in Ref. 21.

Several spectra published in this article could not be reproduced and are unpub-
lished.

The present designations rely on the state the selection rules
$\Delta K_z = \text{odd}$, $\Delta K_z = \text{odd for } \ell = \text{even}$, a result that is not compatible with Eqs. (3) and (4).

The nomenclature used here to designate the electronically excited states of allyl ($\tilde{A}^1B_1, \tilde{B}^1A_1, \tilde{C}^1B_1, \tilde{D}^1A_1, \tilde{E}^1B_1$) differs from that used in Refs. 1 and 2 ($\tilde{A}^2B_1, \tilde{B}^2A_1, \tilde{C}^2B_1, \tilde{D}^2A_1, \tilde{E}^2B_1$). The present designations rely on the energetic ordering and symmetry assignments made in Ref. 21.

References