Deceleration and trapping of a fast supersonic beam of metastable helium atoms with a 44-electrode chip decelerator

Journal Article**Author(s):**

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Publication date:

2013-10

Permanent link:

<https://doi.org/10.3929/ethz-a-010803674>

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Originally published in:

Physical Review A 88(4), <https://doi.org/10.1103/PhysRevA.88.043433>

Funding acknowledgement:

135342 - Rydberg states, VUV laser spectroscopy and photoionization dynamics (SNF)

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The following article appeared in *J. Chem. Phys.* **139**, 084308 (2013) and may be found at <https://aip.scitation.org/doi/10.1063/1.4818982>.

On the adiabatic ionization energy of the propargyl radical

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(Dated: 19 November 2019)

The photoionization and pulsed-field-ionization zero-kinetic-energy-photoelectron spectra of the propargyl radical have been recorded in the vicinity of the origin of the $\tilde{X}^+ \ ^1A_1 \leftarrow \tilde{X} \ ^2B_1$ photoionizing transition. An internally cold sample of propargyl with a rotational temperature of ~ 45 K was produced in a supersonic expansion of 1,3-butadiene in helium. Propargyl was generated by excimer laser (ArF, 193 nm) photolysis of 1,3-butadiene in a quartz capillary mounted at the exit of a pulse valve. The rotational structure of the origin band of the photoelectron spectrum was partially resolved and an improved value of the adiabatic ionization energy of propargyl ($E_I/hc = 70174.5(20) \text{ cm}^{-1}$) was determined.

PACS numbers: Add Pacs

Keywords: C₃H₃, propargyl, photolysis, photoionization, PFI-ZEKE photoelectron spectroscopy, ionization energy

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I. INTRODUCTION

The propargyl radical, $\text{HC}\equiv\text{C}-\dot{\text{C}}\text{H}_2$ (C_3H_3) is one of the simplest organic radicals with a conjugated π -electron system. It is encountered in combustion plasmas and is an important intermediate in chemical reaction systems that lead to the formation of benzene, other aromatic molecules, and, under appropriate conditions, even soot.¹⁻³

For these reasons considerable efforts have been invested to produce and detect this radical in the gas phase, to study its electronic structure, to establish reliable procedures to measure its concentration and to determine basic thermochemical quantities, such as its adiabatic ionization energy, needed to model chemical processes in flames.¹ Four independent measurements of the adiabatic ionization energy of propargyl have been reported since 2006, two with an uncertainty of 160 cm^{-1} ^{4,5} and two with much smaller uncertainties of 8 cm^{-1} ⁶ and 4 cm^{-1} ⁷, but differing by almost 200 cm^{-1} (see Table III). Ref.⁷ makes it clear that the latter result, i.e., $70156(4)\text{ cm}^{-1}$, obtained by velocity-map-imaging threshold photoelectron spectroscopy is the more reliable one. The two most recent high-level *ab initio* calculations of the adiabatic ionization energy^{8,9} yielded values differing by more than 50 cm^{-1} , but both in favor of the value determined by Gao *et al.*⁷.

We report here on a new determination of the adiabatic ionization energy of propargyl based on high-resolution measurements of the photoionization and the pulsed-field-ionization zero-kinetic-energy photoelectron spectra of propargyl and discuss possible reasons for the discrepancy between our new result and the results reported in Refs. 6 and 7.

II. EXPERIMENT

The experiments were performed using a broadly tunable narrow-bandwidth vacuum-ultraviolet laser coupled to a pulsed-field-ionization zero-kinetic-energy photoelectron spectrometer described in Refs. 10 and 11.

The propargyl radicals were produced by 193 nm laser photolysis of 1,3-butadiene in a 1:10 mixture in He using an ArF excimer laser, following the method described in Ref. 12. The photolysis was carried out in a quartz capillary located at the exit of a pulsed valve. The supersonic beam formed by adiabatic expansion at the end of the capillary was skimmed prior to entering the photoelectron spectrometer, where it was crossed at right angles by the VUV laser beam on the axis of set of resistively coupled cylindrical ion/electron extraction plates. The rotational temperature of the radicals in the supersonic beam was found to be about 45 K from the analysis of the rotational

structure of the photoelectron spectra.

The VUV laser radiation was generated by resonance-enhanced difference-frequency mixing in a gas cell filled with Kr at a pressure of 65 mbar, as described in Ref. 10. The calibration of the VUV wave number was performed at an accuracy of 0.02 cm^{-1} .

The photoionization spectrum was recorded by monitoring the ions produced by photoionization as a function of the VUV wave number. The ions were extracted toward a microchannel-plate (MCP) detector by a pulsed electric field of 166 V/cm applied 800 ns after photoionization.

PFI-ZEKE photoelectron spectra were measured by using a two-pulse electric-field sequence consisting of a discrimination pulse of 33 mV/cm followed by a field ionization pulse of -830 mV/cm which also extracted the electrons toward the MCP detector. The narrowest lines observed experimentally had a full width at half maximum of 1.5 cm^{-1} , limited by spectral congestion. The field-induced shift of the ionization threshold was compensated as described in Ref. 11.

The gas pulses, the laser pulses, the electric-field pulses and the detection electronics were triggered at a repetition rate of 25 Hz and were synchronized using delay generators.

III. ROTATIONAL STRUCTURE AND PHOTOIONIZATION SELECTION RULES

Neutral propargyl and its cation are both near-prolate asymmetric-top molecules. Their structure is represented schematically in Fig. 1 which also defines the molecule-fixed axis system used in this work and which corresponds to the convention I^r ,¹³ with the a and b axis in the plane of the molecule. The molecular symmetry appropriate to label the rovibronic energy levels of the neutral molecule and the cation at the resolution of our experiments is $C_{2v}(M)$.¹⁴ The rotational constants of the vibronic ground state of propargyl have been determined experimentally by Tanaka *et al.*¹⁵ and those of the cation have been calculated by Huang *et al.*¹⁶ Their values are listed in Table I with the corresponding asymmetry parameter κ ($= (2B - A - C)/(A - C)$).

The ground electronic state of propargyl has 2B_1 symmetry and the singly occupied molecular orbital is a conjugated π -type orbital of b_1 symmetry with a nodal plane in the molecular plane. Removal of the unpaired electron leads to the formation of the electronic ground state of the cation which has 1A_1 electronic symmetry.

Because we could not resolve the spin-rotational splittings of the rotational levels of the

neutral ground state we used the $|NKM\rangle$ symmetric-top basis to compute the rotational level structure of both neutral and cation, where N is the rotational quantum number and K and M are the quantum numbers associated with the projection of $\vec{N}$ onto the a -axis and onto the Z -axis of the space-fixed coordinate system, respectively. To distinguish the quantum numbers of the neutral and ionized molecule we use the superscripts $''$ and $^+$, respectively. At the low rotational temperature of the radicals in the supersonic beam (≈ 45 K), a rigid-rotor Hamiltonian represented an adequate description of the observed structures.

The rotational levels were classified according to the even (e) or odd (o) nature of K_a and K_c , as summarized in Table II. K_a and K_c represent the asymmetric-top quantum numbers associated with the projection of $\vec{N}$ onto the a and c axes of the molecule, respectively.

From the general rovibronic photoionization selection rules¹⁷

$$\Gamma_{\text{rve}}(\text{neutral}) \otimes \Gamma_{\text{rve}}(\text{ion}) \supset \Gamma^* \text{ for } \ell \text{ even} \quad (1)$$

and

$$\Gamma_{\text{rve}}(\text{neutral}) \otimes \Gamma_{\text{rve}}(\text{ion}) \supset \Gamma^{(s)} \text{ for } \ell \text{ odd}, \quad (2)$$

where Γ^* and $\Gamma^{(s)}$ are the dipole-moment representation (A_2) and the totally symmetric representation (A_1), respectively, one obtains the following restrictions on the changes of K_a and K_c resulting from photoionization

$$\left. \begin{aligned} \Delta K_a &= K_a^+ - K_a'' = \text{odd} \\ \Delta K_c &= K_c^+ - K_c'' = \text{even} \end{aligned} \right\} \text{ for } l \text{ even} \quad (3)$$

and

$$\left. \begin{aligned} \Delta K_a &= \text{odd} \\ \Delta K_c &= \text{odd} \end{aligned} \right\} \text{ for } l \text{ odd}. \quad (4)$$

Assuming that the b_1 orbital from which the electron is ejected has a dominant p character, angular momentum conservation rules¹⁸ indicate that the dominant transitions should conform to

$$\Delta N = N^+ - N'' = 0, \pm 1, \pm 2. \quad (5)$$

Moreover, the removal of an electron from an orbital with a nodal plane containing the a axis implies the selection rule $\Delta K_a = \pm 1$.

The transitions originating from levels of even (odd) K_a'' values were weighted by a factor of 3 (1) corresponding to the spin-statistical weights of the rotational levels.

IV. RESULTS AND DISCUSSION

The PFI-ZEKE photoelectron spectrum of the origin band of the $\tilde{X}^+ {}^1A_1 \leftarrow \tilde{X} {}^2B_1$ photoionizing transition is depicted in Fig. 2a, where it is compared with a calculated spectrum assuming a rotational temperature of 45 K and using weighting factors of 1, 2 and 0.7 for the branches with $\Delta N = 0, \pm 1$ and ± 2 , respectively. These assumptions led to the stick spectrum depicted in Fig. 2b.

The spectrum displayed as thick red line in Fig. 2a was obtained by convolution of this stick spectrum with a Gaussian line-shape function with a full width at half maximum of 1.5 cm^{-1} . The dominant pattern of the PFI-ZEKE spectrum is the series of five regularly spaced narrow lines which correspond to $\Delta N = 0$ branches associated with all possible $|\Delta K_a| = 1$ transitions accessible from the $K_a'' = 0-2$ levels populated in the ground state. The strongest of these lines is that originating from $K_a'' = 0$ levels which are the most populated levels at 45 K.

The PFI-ZEKE photoelectron signal was found to be extremely weak and, consequently, several spectra recorded under identical conditions had to be added to obtain a signal-to-noise ratio high enough to unambiguously identify the five expected $\Delta N = 0$ branches corresponding to the five $|\Delta K_a| = 1$ transitions. In their study of VUV-VMI-TPE spectrum of propargyl, Gao *et al.* also noted the weakness of the PFI-ZEKE photoelectron signal which prevented them from recording the PFI-ZEKE photoelectron spectrum of propargyl.⁷ Because the photoionization signal of propargyl is strong, we suspect that the high-Rydberg states of propargyl that are detected in the PFI-ZEKE photoelectron spectroscopic experiments are partially depleted by predissociation before the field ionization pulse is applied.

The resolution of the spectrum and the low signal-to-noise ratio prevented the observation of individual rotational lines. Fortunately, the sharpness of the $\Delta N = 0$ branches enabled the precise determination of the adiabatic ionization threshold $E_I/hc = 70174.5(20) \text{ cm}^{-1}$ and of the A_0^+ constant ($A_0^+ = 9.37(5) \text{ cm}^{-1}$) which lies close to the value calculated *ab initio* (see Table I).¹⁶

The $\Delta N = 1$ branch located on the high wave-number side of the central $K_a'' = 0 \rightarrow K_a^+ = 1$ line is broader than the $\Delta N = -1$ branch located on its low wave-number side which suggests that the B_0 and the C_0 constants are larger in the cation than in the neutral molecule, which is also in accord with the values presented in Table I. The values of B_0^+ and C_0^+ used to calculate the spectrum displayed in Fig. 2a were 0.32 cm^{-1} and

0.31 cm⁻¹, respectively, but could not be fitted because of the low signal-to-noise ratio of our spectrum.

In Table III, the value of the adiabatic ionization energy of propargyl determined from the PFI-ZEKE photoelectron spectrum is compared with the most recent values of this quantity reported in the literature. Our new value lies within the error bars of 160 cm⁻¹ of the previous measurements by threshold photoelectron spectroscopy (TPES)⁴ and photoionization mass spectrometry (MT-RPMS).⁵ It is a factor of 2 and 4 more precise than the two most precise earlier experimental values, obtained by velocity-map imaging threshold photoelectron spectroscopy⁷ and photoionization spectroscopy,⁶ respectively, and lies significantly above both.

The value of 69961(8) cm⁻¹ reported in Ref. 6 was obtained from the position of a weak step in the photoionization spectrum of propargyl recorded with synchrotron radiation and an effusive source of C₃H₃ radicals produced by 193 nm ArF excimer laser photolysis of propargyl chloride. The discrepancy between this value and the present one may be related to the elevated temperature of the propargyl sample used in Ref. 6, an argument that was already used in Ref. 7 to explain the difference between the results reported in Refs. 7 and 6. The value of 70156(4) cm⁻¹ reported in Ref. 7 was derived from a vacuum-ultraviolet-velocity-map-imaging threshold photoelectron (VUV-VMI-TPE) spectrum after having calibrated the shift of the ionization thresholds under their experimental conditions from an independent set of measurements of the adiabatic ionization energy of C₆H₅Cl. The discrepancy with the present result may have its origin in a systematic error in the adiabatic ionization energy of C₆H₅Cl used as reference or in a systematic error associated with the determination of the origin of the photoelectron band from the structured rotational envelope of this band (see Fig. 3 of Ref. 7).

In their analysis, Gao *et al.* used the same rovibronic photoionization selection rules as we did. The main differences between the two analyses are that the intensities of the rotational branches with $\Delta N = -3, -2, -1, 0, 1, 2$ and 3 were weighted by the factors 2, 3, 4, 6, 5, 3 and 2, respectively, in Ref. 7 and by 0, 0.7, 2, 1, 2, 0.7 and 0 in the present work, and that we weighted the transitions originating from levels with odd and even values of K_a by nuclear-spin-statistical weights of 1 and 3, respectively, while the opposite weights were used in Ref. 7. It is conceivable that the different spin-statistical weights used in the two analyses are responsible for the difference in the ionization energies. With the spin-statistical weights used in the present work, the most intense transitions are those originating from $K_a'' = 0$ levels whereas those originating from $K_a'' = 1$ levels are

the most intense if the opposite weights are used¹⁹. The fact that we can resolve the five $\Delta N = 0$ branches in our PFI-ZEKE photoelectron spectrum leaves little doubt concerning the correctness of the present analysis and of our new value of the ionization energy of propargyl.

To further test the validity of the present result, we also recorded the photoionization spectrum of propargyl. The spectrum displayed in Fig. 3, was obtained using a pulsed electric field of 166 V/cm delayed by 800 ns with respect to the photoexcitation laser pulse. The normalized C_3H_3^+ signal rises from the background level of 0.1 to 1 over the spectral range where a measurable PFI-ZEKE photoelectron signal could be detected (see Fig 2). The photoionization spectrum turned out to be independent of the value of the pulsed electric field used to extract the C_3H_3^+ ions. We attribute this observation to the rapid predissociation of the Rydberg states of propargyl already noted above. The adiabatic ionization energy determined from the PFI-ZEKE photoelectron spectrum is marked by the vertical line in Fig. 3 and crosses the photoionization curve at mid-rise, as expected.

V. CONCLUSIONS

The high-resolution PFI-ZEKE photoelectron spectrum of propargyl has been recorded following single-photon excitation from a cold sample of the radical in a supersonic expansion. The PFI-ZEKE photoelectron spectrum was found to be extremely weak, which suggests that the Rydberg states of propargyl are predissociative in the region of the first ionization threshold.

The observation of sharp lines corresponding to the $\Delta K_a = \pm 1$ and $\Delta N = 0$ rotational branches enabled the determination of an improved value of the adiabatic ionization energy of propargyl ($E_I/hc = 70174.5(20) \text{ cm}^{-1}$). Possible origins of the discrepancies with previous results were discussed.

ACKNOWLEDGEMENTS

We thank Prof. P. Chen and Dr. A. Bach (both ETH Zürich) for useful discussions and their encouragements and Prof. C.Y. Ng (University of California, Davis) for communicating the revised simulation of the photoelectron spectrum published in Ref.⁷ after we had sent him a preprint of the present work. This work was supported financially by the Swiss National Science Foundation under project Nr. 200020-135342.

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FIG. 1. Schematic representation of the propargyl radical and definition of the principal-axis system (convention I^r).

FIG. 2. a) Comparison of the experimental (black) and calculated (red) PFI-ZEKE PE spectrum of the $\tilde{X}^+ {}^1A_1 \leftarrow \tilde{X}'' {}^2B_1$ transition of the propargyl radical. b) Calculated stick spectrum of the $\tilde{X}^+ {}^1A_1 \leftarrow \tilde{X}'' {}^2B_1$ transition of the propargyl radical. The red curve in panel a) corresponds to the convolution of the stick spectrum in panel b) with a Gaussian line-shape function (FWHM = 1.5 cm^{-1}).

FIG. 3. Photoionization spectrum of the propargyl radical. The vertical line represents the adiabatic ionization threshold determined from the PFI-ZEKE photoelectron spectrum (see text).

TABLE I. Rotational constants of the vibronic ground state of the neutral propargyl radical and the propargyl cation from Refs. 15 and 16, respectively.

	$\tilde{X}'' \ ^2B_1$	$\tilde{X}^+ \ ^1A_1$
A_0 (cm $^{-1}$)	9.60848(5)	9.45158
B_0 (cm $^{-1}$)	0.3176757(2)	0.32312
C_0 (cm $^{-1}$)	0.3071085(2)	0.31201
κ	-0.998	-0.998

TABLE II. Rovibronic symmetries of the $N''_{K_a''K_c''}$ and $N^+_{K_a^+K_c^+}$ rotational levels of the propargyl radical and its cation in the $C_{2v}(M)$ point group and nuclear-spin-statistical weights of the neutral rovibronic levels.

K_aK_c	$\Gamma_{\text{rve}}(\text{C}_3\text{H}_3)$	Spin-statistical weight	$\Gamma_{\text{rve}}(\text{C}_3\text{H}_3^+)$
ee	B_1	3	A_1
eo	B_2	3	A_2
oe	A_2	1	B_2
oo	A_1	1	B_1

TABLE III. Comparison of the present value of the adiabatic ionization energy of the propargyl radical with previous results. (VMI-TPES: velocity-map-imaging-threshold photoelectron spectroscopy, VUV-PIS: vacuum-ultraviolet photoionization spectroscopy, MT-RPMS: multiplexed time-resolved photoionization mass spectrometry, TPES: threshold photoelectron spectroscopy, PES: photoelectron spectroscopy)

$E_I/[(hc) \text{ cm}^{-1}]$	Ref.	Method
70156(4)	7	VUV-VMI-TPES
69961(8)	6	VUV-PIS
70170(160)	5	MT-RPMS
70251(160)	4	TPES
69928(160)	20	PES
70162, 70210	8	<i>ab initio</i>
70219	9	<i>ab initio</i>
70174.5(20)	this work	PFI-ZEKE PES