Femtosecond pump–probe photoelectron spectroscopy of predissociative Rydberg states in acetylene

S. L. Sorensen
Department of Synchrotron Radiation Research, Lund University, Box 118, 221 00 Lund, Sweden

O. Björneholm, I. Hjelte, T. Kihlgren, G. Öhrwall, S. Sundin, and S. Svensson
Department of Physics, Uppsala University, Box 530, 751 21 Uppsala, Sweden

Department of Physics, Lund Institute of Technology, Box 118, 221 00 Lund, Sweden

(Received 26 October 1999; accepted 11 February 2000)

We employ a pump–probe approach to molecular photoionization to study fast dissociation of Rydberg states in acetylene. By using time-resolved photoelectron spectroscopy to study the electronic state of the resulting ions we are able to monitor the system continuously during dissociation or rearrangement. We find that the predissociative lifetime for the 3R" (ν₁ = 1) Rydberg state is about 150 fs. We demonstrate a powerful new technique using time-correlated femtosecond harmonic generation and laser light pulses to study the time evolution of ultrafast dynamic processes in molecules. © 2000 American Institute of Physics.

INTRODUCTION

The photochemistry of acetylene in the vacuum ultraviolet region is widely studied within the context of planetary and atmospheric chemistry, combustion dynamics, and as a model for other hydrocarbons. Acetylene is particularly interesting because of its high symmetry, linear geometry, and because of the relatively high abundance of acetylene and ethynyl in planetary atmospheres and interstellar clouds. The lifetimes and reaction dynamics of acetylene and its primary fragments are thus the focus of innumerable studies including vacuum ultraviolet (VUV) absorption spectroscopy, multiphoton ionization, photofragment translational spectroscopy, fluorescence emission spectroscopy, and a large number of calculations. A number of recent studies concentrate upon fast dissociation from low-lying Rydberg states in acetylene by using photofragment action spectroscopy. Although pump–probe spectroscopy on the picosecond level has been in use for a number of years, recent developments in laser technology make real-time femtosecond pump–probe studies of molecular dynamics possible. A number of techniques in which femtosecond lasers are combined with charged-particle detection have provided important information about molecular dissociation and cluster dynamics. The majority of these techniques rely upon multiphoton excitation. The purpose of the present work is to demonstrate a new experimental technique, which provides a detailed picture of the dissociation dynamics of acetylene, as well as of the electronic state in the fragment.

Our method uses femtosecond VUV pulses from a harmonic generation source to pump to the excited Rydberg state. The excited state is probed by a second short laser pulse which photoionizes the prepared electronic state after a given time interval. By analyzing the kinetic energy of emitted photoelectrons the state of the system at the moment of ionization is determined. In the present work, we employ this pump–probe technique to investigate the dynamics of the linear 1Σ⁺ 3d π 3R" (ν₁ = 1) Rydberg state at 9.43 eV. The VUV pump pulse is provided by the sixth harmonic of a 789.5 nm 120 fs titanium-sapphire laser. The harmonic radiation is generated in the interaction of the frequency-doubled laser light with a gas jet of xenon atoms. The probe pulse is a fraction of the frequency-doubled laser light. The time delay between the two pulses can be continuously varied. Because of a perturbation from the close-lying non-linear E valence state this Rydberg state is highly dissociative. For a short pump pulse we find a number of peaks with a kinetic energy below that which corresponds to the adiabatic transition to the X state of the acetylene ion. These peaks show different intensity variations as the delay time increases.

Techniques such as laser-induced fluorescence or ion yield spectroscopy probe the state of the system at an unspecified time after the photoexcitation. Photoelectron spectroscopy has an advantage in that it is possible to obtain information about the state of the system at the instant of photoionization. In addition, since the final electronic state for photoionization is in the continuum, the spectra are relatively simple to interpret. High-resolution spectra allow information about bond-length changes and dissociation to be extracted directly. The decay life time of the peak arising from ionization from the Rydberg state is found to be 150 fs which is in agreement with recent atom action spectroscopy measurements of the states near 9.43 eV. The combination of short-pulse pump–probe techniques with photoelectron spectroscopy is a promising technique for studies of fast molecular dissociation.
is split into two infrared pulses of equal energy. Both pulses of 3.14 eV, we proceed in the following way. The laser pulse rate.

The experimental setup is shown in Fig. 1. Using the terawatt laser at the Lund high-power laser facility, infrared pulses are generated with a time duration of 120 fs. The laser light has a wavelength of 789.5 nm ($h
\nu = 1.57\text{ eV}$) and the pulse energy is a few tens of mJ at a 10 Hz repetition rate.

To produce a pump pulse of 9.42 eV and a probe pulse of 3.14 eV, we proceed in the following way. The laser pulse is split into two infrared pulses of equal energy. Both pulses are frequency doubled in two KDP (potassium dihydrogen phosphate) crystals (see Fig. 1) and recombined with the help of another beam splitter (BS). One arm of the setup is mounted on a translation stage with micrometric resolution to allow for variable time delay. This setup also allows us, with few modifications, to produce pairs of pulses with variable relative time delay at infrared (1.57 eV), blue (3.14 eV), or ultraviolet (4.71 eV) photon energies (or any combination of these energies).

One of the blue pulses is focused by a lens ($f = 2\text{ m}$) into a pulsed jet of xenon atoms, where the sixth and tenth harmonics of the fundamental frequency are efficiently produced by third and fifth harmonic generation. As described below, the tenth harmonic (15.7 eV photon energy) is used to obtain a reference (one color) spectrum. This spectrum provides information about the purity of the sample, alignment, space-charge effects and to some degree, a diagnostic of the harmonic radiation. The sixth harmonic (9.42 eV) is our pump pulse. In the pump–probe experiment, we eliminate the tenth harmonic by inserting a LiF window absorbing radiation with wavelength below 105 nm (11.8 eV). However, the blue radiation originating from the same pulse is not eliminated, but the intensities in the gas cell are not sufficient to induce any multiphoton process. The infrared radiation is eliminated with the help of a polarizer, $P$ (Fig. 1). Since the ionization energy of acetylene is above the LiF cut-off energy, we ionize the sample only when the pump and probe pulses are properly synchronized.

The second pulse, which is our probe radiation (3.14 eV), is focused just before the gas cell of the electron spectrometer by a lens combination as in Fig. 1. It is not focused in the center of the gas cell in order to avoid multiphoton ionization of the sample as well as to maximize the spatial overlap with the pump beam in the interaction volume. The peak intensity of this radiation when passing the xenon gas jet is not high enough to generate harmonics.

The electron spectrometer is a truncated hemispherical electrostatic analyzer employing a retarding lens and a two-dimensional multichannel detection system. The detector consists of a matched set of microchannel plates with a phosphor screen. It is possible to register the entire 5 eV kinetic-energy region simultaneously in each measurement, but in order to distribute the signal evenly over the utilized area of the detector the lens potentials are swept and the signal is summed in each channel. Each event is recorded using a video camera and the integration of signal is made on the camera and charge-coupled device array. This multichannel electron detection allows us to effectively compensate for the relatively low spectrometer transmission. The spectrometer FWHM (full width at half maximum) employed in this study is $\sim 75\text{ meV}$. The source is a continuously pumped gas cell with a pressure of $\sim 0.01\text{ mbar}$. The background pressure is $3.0 \times 10^{-8}\text{ mbar}$.

The pulsed light source creates a time-dependent potential from the ions created by photoionization. This potential can lead to line broadening and energy shifts in the measured electron spectra. The magnitude of the space-charge potential depends principally on the number of ions and can be minimized by controlling the gas pressure.

Since the kinetic energy of the electrons leaving the sample depends upon both the electronic state of the electrons and upon the energy of the ionizing radiation we can distinguish between photoelectrons from different potential surfaces by analyzing the kinetic energy. For single-photon ionization to the ground state of $\text{C}_2\text{H}_2$ a spectrum is produced with peaks corresponding to vibrational levels in the final-state potentials, and the energy depends upon the difference between the neutral ground state and the final ionic state. For pump–probe ionization the difference between the ionized state and the bound state of the electrons at the moment of ionization is measured. This is of great importance for these studies.

**RESULTS**

We begin with a single-photon photoelectron spectrum of acetylene. The ground-state configuration of acetylene is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(3\sigma_g)^2(1\pi_u)^2X^1\Sigma_g^+$. The ground $^2\Pi_u$ state of the acetylene ion is linear with an adiabatic binding energy of 11.403 eV. The kinetic energy spectrum corresponding to this final state using the tenth harmonic at 15.70 eV is shown in Fig. 2. The photon bandwidth is approximately the same as the full width half maximum of the spectrometer transmission function. The main peak observed in the spectrum corresponds to the lowest vibrational level of the $X$ state. Peaks reflecting excitation of the $\nu_2$ C–C stretch mode and of the $\nu_4$ bending mode are present and are indicated by the ladder in Fig. 2(a). These vibrational features are well known and the spectrum closely resembles pub-
lished spectra of comparable resolution. As a rule the kinetic energy of emitted photoelectrons for a given system depends solely upon the photon energy and the electronic final state. This is not the case when an intermediate state is included in the study. Changes in kinetic energy as a function of pump–probe delay time reflect dynamics such as dissociation or geometrical changes in the intermediate state. This should be kept in mind when examining the spectra.

Some spectra from pump-probe ionization are shown in Fig. 2(b). Notice the difference in kinetic energies between Figs. 2(a) and 2(b). The first spectrum is obtained with 15.70 eV photons, whereas the other spectra involve a two-color process with a total excitation energy which is 3.14 eV lower. For the 0 fs delay spectrum the energy of the higher kinetic-energy peak corresponds to the adiabatic peak in Fig. 2(a). This peak is indicated with a solid bar in the lower part of the figure.

The spectra for pump–probe time delays varied from −120 to +600 fs are included in the plot. The spectra are scaled to approximately equal height. The zero time delay was determined as the time delay that resulted in the strongest signal corresponding to ionization of molecular acetylene. The spectra in the figure are scaled to the same arbitrary height for comparison although in reality there is a large dynamic range through the series. There are a number of dramatic changes in the peak structure of the photoelectron spectrum. The short delay spectra exhibit only minor differences when compared with the single-photon spectrum in Fig. 2(a). In particular, the adiabatic peak at 1.16 eV kinetic energy remains a significantly strong feature. We propose that the spectra measured with two nearly simultaneous pulses contain mainly photoelectrons from the $X^2\Pi_u$ state of the acetylene ion. We attribute the slight differences between the weights of the different electron peaks in the one-color spectrum compared to the first two-color spectra to be mostly due to the difference in the excitation process. The vibrational structure in the final state reflects the Franck–Condon factors between the initial and the final states. The two-color process involves a product of the two Franck–Condon factors for the excitation and for the ionization. In the uppermost spectrum the probe pulse precedes the pump pulse by ~120 fs. Obviously the temporal overlap of the two pulses is sufficient already to ionize a number of molecules. As the pulses overlap more completely the intensity of the main (adiabatic) peak at 1.16 eV kinetic energy reaches a maximum at delay 0 fs.

As the delay between the pump and the probe pulses increases the absolute intensity of the adiabatic peak at 1.16 eV decreases rapidly. Its temporal evolution is shown in Fig. 3 (full circles). If we account for the temporal widths of both pump and probe pulses (estimated to 120 fs for each pulse), a fit of the experimental curve (solid line) leads to an exponential decay for the excited Rydberg state of 150 fs. This value is in agreement with spectral width measurements by hydrogen atom action spectroscopy. As the time delay increases additional peaks at 0.96 and 0.87 eV kinetic energy arise, before decreasing at a less rapid rate. The behavior of the 0.96 eV peak (open circles) is interesting since at least part of the intensity should arise from the time-dependent geometry changes in the acetylene molecule. The intensity of the peak should depend upon two processes: The vibrational peak of the $C_2H_2^+$ $X$ state, and an unidentified peak in the product spectrum. Because of the ambiguity in the Franck–Condon factors for the $X$ state it is impossible to correctly attribute the intensity to a vibrational level in the $C_2H_2^+$ $X^2\Pi_u$ state or to a state belonging to another geometry. Unfortunately we were unable to describe the time-dependent behavior of this peak using the same method as for the 1.16 eV peak based upon an exponential decay of the excited state. We conclude that such analysis relies upon accurate information about Franck–Condon factors or better energy resolution in the spectrum.
DISCUSSION

It is well established that the $^1\Pi_g\, 3d\sigma_g\, 3R'$ ($v_2 = 1$) and $^1\Sigma_u^+\, 3\pi\, 3R''$ ($v_2 = 1$) Rydberg states decay very rapidly by dissociation \cite{4,8,10} and several explanations for this short dissociative lifetime have been presented. The Rydberg states are certainly strongly perturbed since they are crossed by a repulsive state. Our spectra indicate that ionization via the Rydberg states leads to different state configurations as the wave packet propagates on the potential surface. We find a predissociation time of 150 fs which characterizes the time scale for the disappearance of the wave packet from the Franck–Condon region described by the ground state which is in accord with our results. Identifying the fate of this predissociation is somewhat more difficult.

Based upon the 150 fs time scale we may make some assumptions regarding the dynamics of the excited state. Fluorescence decay takes place on a time scale of picoseconds. We find such decay processes of minimal importance in our spectra since the time scale is distinctly shorter. On the other hand vibrational periods are somewhat shorter than the 150 fs time scale. We thus exclude fluorescence and vibrational effects from the probable cause of the spectral changes observed in our study. Rearrangement and dissociation are processes most likely to lead to changes on this time scale.

For time delays greater than 300 fs the signal becomes very weak. We have made a check of the timing of the pulses and the possibility of excitation by stray light or other sources has been eliminated. We discuss the interpretation of these spectra below based upon the formation of an intermediate state which decays on a relatively short time scale.

CONCLUSIONS

Using short-pulsed VUV radiation from harmonic generation to pump Rydberg states in acetylene and femtosecond laser light to photoionize from the dissociating state we find a predissociation lifetime of 150 fs for the $^1\Sigma_u^+\, 3\pi\, 3R''$ ($v_2 = 1$) state. The time-resolved spectra also contain peaks arising from the result of the predissociation. Higher resolution measurements are needed to ascertain the nature of these fragments.

ACKNOWLEDGMENTS

Support from the Göran Gustafsson Foundation for research in natural sciences and medicine, from the Swedish Natural Science Research Council and the European Community is gratefully acknowledged. D.D. is supported by a TMR Marie Curie grant from the European Community (ERBFMBICT 983348). A.L. thanks D. Gauyacq and B. Girard for stimulating discussions.

The well-studied C_2H+H photolysis channel is the most relevant to this study. The ground state of the C_2H radical ($X^2\Sigma^+$) and the $A^2\Pi$ state have been identified \cite{21,22} (0.45 eV) and dissociation thresholds for these processes are measured. The bond dissociation energy is found to be 5.71 eV \cite{21} and the ionization potential of ethynyl is 11.71 eV.\cite{23} From the C_2H+H dissociation energy we can fix the ground state of ethynyl if we assume that no kinetic energy is released. Thus the excited state of importance would lie ~3.7 eV above the ethynyl ground state. Given the ionization energy of ethynyl at 11.61 eV \cite{23} such a state would not be accessible with one 3.14 eV energy photon. Despite independent evidence for this dissociation pathway \cite{8,9} we must exclude the ethynyl fragment from our analysis.

Rearrangement processes could also explain the 0.96 eV peak. Vinylidene is a possible candidate. Experimental evidence indicates that the ionization potential for vinylidene lies ~2 eV above that of acetylene \cite{24} but little is known about excited states lying within 3 eV of the ionization potential. Vinylidene is unstable; photoelectron measurements of negative ions lead to a lower limit of 0.013 ps for the lifetime of the molecule. This makes it an unlikely candidate for the 0.96 eV peak in our spectrum.

The peaks at lower kinetic energies (220 and 90 meV lower kinetic energy) have energy splittings very close to the C–C stretch and the trans bending mode and could be interpreted as vibrational peaks for C–C stretch and bending modes in an isotope or fragment. The statistics in the lower spectrum (600 fs delay) where this structure is clearest are not good and further measurements are necessary in order to develop this speculative interpretation.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Intensities of the 1.16 eV peak as a function of the delay between the pump and probe laser pulses (solid circles). The solid line represents a double convolution of two 120 fs pulses (hyperbolic secant) with an exponential decay function. The best agreement with the measured data is obtained for a decay lifetime of 150 fs.}
\end{figure}