Constant photoelectron energy spectroscopy of acetylene

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Constant photoelectron energy (CPE) spectra of acetylene are reported for electron kinetic energies of 0, 0.1, 0.5, and 1.0 eV in the spectral range $11 \leq h\nu \leq 22$ eV. This form of photoelectron spectroscopy involves measuring the intensity of photoelectrons with a particular kinetic energy as a function of the wavelength of the incident radiation. Such measurements may be carried out using small wavelength increments and can distinguish between direct and indirect, e.g., autoionization and photoionization processes. Autoionization features in the range $12.5 \leq h\nu \leq 16$ eV are observed, which populate high vibrational levels of the ground state far beyond the Franck–Condon region.

I. INTRODUCTION

Photoelectron spectroscopy is a well-established technique, which, nevertheless continues to evolve as technical developments, scientific demands, and new configurations emerge. Hence, the measurement of photoelectron angular distributions and the advent of synchrotron radiation as a continuously tunable excitation source (see, e.g., Ref. 1) have enhanced the power of photoelectron spectroscopy from the original fixed-angle, resonance lamp configuration. Triply differential photoelectron spectroscopy (differential in wavelength, kinetic energy, and ejection angle) is in principle capable of mapping the photoionization process as a smooth function of all three independent variables. In practice, however, the intensity of suitably monochromated continuum light sources combined with the small acceptance angle of most energy analyzers have resulted in somewhat coarse coverage of the wavelength scale. Here we use an alternative mode of electron spectroscopy—constant photoelectron energy (CPE) spectroscopy—which constrains the photoelectron kinetic energy to selectable but *fixed* values and monitors the photoelectron intensity as an incremental function of incident wavelength. This procedure is not strictly new, as it has been employed in a similar form in solid state physics. The present usage emphasizes aspects which are complementary to related experimental techniques: e.g., threshold photoelectron spectroscopy (TPES).[2–7] Threshold photoelectron spectroscopy in which electrons having essentially *zero* energy are detected, has been used for several years to determine molecular energy levels and investigate autoionization effects. CPE spectroscopy is also closely related to two other techniques, constant initial state (CIS) spectroscopy and constant final state (CFS) spectroscopy.[8] In CIS spectroscopy, the photon energy and the electron spectrometer analysis energy are swept synchronously so that electrons ejected from a particular molecular orbital state are monitored. In this manner, the photoionization cross section for a chosen state is measured as a function of photon energy. Plummer *et al.*[9] have employed CIS spectroscopy to determine electron partial cross sections for specific molecular orbitals in N_2 and CO. In CFS spectroscopy, the electron analysis energy is fixed and the photon energy is scanned. The experimental procedures for CFS and CPE spectroscopy are the same; however, the term CFS spectroscopy is often applied to cases in which Auger electrons are being analyzed. Hence, in addition to the electrons having a constant kinetic energy, the hole state from which the electrons are being ejected also remains constant.[10] Since CPE spectroscopy is a relatively new technique, especially in its application to gas-phase work, a brief description of the method together with an indication as to the type of information it can provide, appears worthwhile.

CPE spectroscopy can best be explained by consideration of the photoionization energy balance equation

$$E_{ph} = E_I + E_k \ , \tag{1}$$

where E_{ph} is the photon energy, E_I is the ionization potential of a particular orbital in the neutral molecule, and E_k is the kinetic energy carried off by the ejected electron. In CPE spectroscopy, E_k is set by the electron spectrometer. As the photon energy is scanned,

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electrons with a specified E_k will be detected whenever Eq. (1) can be satisfied. For example, if $E_k = 1$ eV, an electron signal will be observed whenever the photon energy is 1 eV greater than a particular vibronic state of the ion. The significance of CPE spectroscopy is twofold: First, direct and indirect photoionization can be distinguished readily. Second, the decay of neutral autoionizing states into non-Franck–Condon regions of the ionic state manifold can be observed directly.

The ability to distinguish between photoionization mechanisms can be explained as follows: In the case of *direct photoionization*, photoelectron peaks will occur at *constant* E_I for those dipole-allowed transitions to vibrational levels of accessible ($E_{ph} > E_I$) ionic states with non-negligible Franck–Condon factors. For *indirect photoionization* via an autoionizing state, photoelectrons will appear at constant E_{ph}, namely, the excitation energy of the quasibound neutral state, subject to the joint condition that the decay leads to a state of the ion such that the photoelectron departs with E_k. This latter constraint is not often difficult, especially when probing the excited vibrational states of polyatomic ions for which the various vibrational modes and their combinations can approach a quasicontinuum.

The second aspect of CPE spectroscopy, emphasized above, concerns the observation of decay of autoionizing states into non-Franck–Condon regions of the vibrational manifolds of ionic states. It is well known from conventional photoelectron spectroscopy that autoionization can induce non-Franck–Condon vibrational intensity distributions. CPE spectroscopy provides a complementary probe to the study of such effects in two ways. First, as previously emphasized, CPE spectroscopy makes practical the continuous variation of wavelength over the autoionization profile. Second, studying the decay as a function of residual kinetic energy can reveal the dynamical effects of electron kinetic energy on the decay process.

In this paper, CPE spectroscopy is applied to acetylene, which has been the subject of many recent studies, both experimental and theoretical. The work most relevant to the present investigation are photoionization yield curves,[11–17] fixed energy (21.2 and 30.4 eV) photoelectron spectra,[18–21] and photoelectron partial cross sections and angular distributions[22–25] using variable photon energy. The structure of this molecule in its linear electronic ground state has the molecular orbital sequence $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$. The experimental values[18] for the three lowest vertical ionization potentials are $(1\pi_u)^{-1}X^2\Pi_u = 11.40$ eV, $(3\sigma_g)^{-1}A^2\Sigma_g = 16.36$ eV, and $(2\sigma_u)^{-1}B^2\Sigma_u = 18.38$ eV. Theoretical predictions for various excited states of the molecule converging onto the A and B state of the ion are given by Hayaishi *et al.*,[16] Langhoff *et al.*,[23] and Machado *et al.*[26] The photoionization spectrum is dominated by resonant structure from threshold to at least 17 eV, but the exact nature of the features, whether they are the result of shape resonances, autoionization, or some combination is still an open question. As CPE spectroscopy is particularly sensitive to autoionization, such a study has been performed on acetylene, in an attempt to provide further insight into this problem. CPE spectroscopy investigates a different cut through the photoionization cross section surface than that studied by conventional photoelectron spectroscopy. In doing so, it generates the cross section for producing electrons with a specific kinetic energy as a function of photon energy. The present experiment covers low kinetic energies ($E_k \leq 1.0$ eV) and provides some distinct features of autoionization in acetylene which we hope will stimulate further theoretical calculations.

II. EXPERIMENTAL

Since CPE data were desired from threshold ($E_k = 0$) to $E_k = 1$ eV, the study was performed on two separate instruments. The threshold photoelectron data ($E_k = 0$) were taken using the electron portion of a photoelectron–photoion coincidence spectrometer[27,28] and a monochromated light source. The remaining data ($E_k \neq 0$) were obtained with a hemispherical electron analyzer[29] coupled to a high aperture 2 m normal incidence monochromator connected to the SURF-II storage ring[31] at the National Bureau of Standards. This arrangement has been used previously to study shape resonance effects (Cole *et al.*,[32] and references therein) and autoionization (Ederer *et al.*,[33] and references therein) in photoelectron spectra. The threshold photoelectron spectrometer possesses an inherently high collection efficiency for zero kinetic energy electrons, but discriminates strongly against energetic electrons. Conversely, the collection efficiency of the hemispherical analyzer is high for energetic electrons but low for near threshold electrons.

The full design details and experimental method for the threshold photoelectron spectrometer have been described previously[27,28] and will only be summarized here. The photon source used was a dc discharge in hydrogen to produce the hydrogen many-line spectrum, and a pulsed discharge in helium to produce the Hopfield continuum. The light was dispersed by a 1 m Seya–Namioka monochromator to give a photon bandwidth of 0.12 nm (FWHM). The intensity was monitored by a tungsten photodiode. The photon beam ionized the acetylene molecules between a series of plane parallel plates. Voltages on the plates accelerated the electrons perpendicular to the photon beam. The electrons passed through a drift tube and entered a 127° cylindrical plate analyzer tuned to pass electrons which had only the energy provided by the electrostatic voltages on the acceleration plates. In this way, electrons produced with zero initial kinetic energy (threshold photoelectrons) were detected, and those produced with excess kinetic energy were discriminated against. The resolution of the photoelectron peak was approximately 28 meV (FWHM).

Both the normal incidence monochromator[30] and the hemispherical electron analyzer[29] have been described previously and will only be outlined here. The monochromator incorporated a 1200 lines/mm osmium coated grating blazed at about 80 nm. The 0.1 mm high electron beam in the storage ring, constituting the entrance

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slit, together with a 0.1 mm exit slit, resulted in a spectral resolution of about 0.05 nm (16 meV at 20 eV), and a photon flux of approximately 5×10^{10} photons/s/bandwidth in the peak of the output for a typical 10 mA circulating beam in the storage ring. The combined resolution of monochromator and electron spectrometer was approximately 110 meV (FWHM). The analyzer consisted of two copper hemispheres of 50 mm mean radius, with zoom lenses which focused the electron source onto a virtual entrance slit, and onto a channeltron detector after energy analysis. The analyzer was operated in a constant pass energy mode of 5 eV, and could be rotated in a plane at right angles to the incident photon beam with an angular acceptance of $\pm2°$. The polarization of the incoming light was measured by a three mirror polarizer[34] which rotated with the electron analyzer.

The photoelectron angular distribution is a function of the kinetic energy of the outgoing electron. In order to obtain meaningful cross sections it is necessary to take this variation into account. The threshold electron collection efficiency is independent of the angular distribution because only zero energy electrons are collected. For elliptically polarized radiation, the differential cross section in the dipole approximation, assuming randomly oriented target molecules, and electron analysis in a plane perpendicular to the photon propagation direction, may be written in the form[35,36]

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_{\text{total}}}{4\pi}\left[1+\frac{\beta}{4}(3P\cos 2\theta+1)\right], \qquad (2)$$

where β is the photoelectron asymmetry parameter, θ is the photoelectron ejection angle relative to the major polarization axis, and $P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$ the polarization of the incoming light. For a particular combination of polarization and ejection angle $(3P\cos 2\theta+1)$ becomes zero, at which point the differential cross section becomes independent of the asymmetry parameter. During the present experiment, the measured polarization was $\simeq 0.57$, so by setting the hemispherical analyzer at $\theta=63°$, the measured differential cross section was directly proportional to σ_{total}.

The computer program which had operated the apparatus in the angularly resolving mode[29] was modified slightly for the CPE spectroscopy, in that the desired initial photon energy and step size, together with the chosen photoelectron kinetic energy had to be specified. The photon energy was gradually incremented over the preselected energy range, while, at the same time, the entrance lens potentials were adjusted so that electrons of the chosen kinetic energy E_k were accelerated or retarded to reach 5 eV, the pass energy of the analyzer. At each photon energy electrons were collected until a certain preset photon count limit was reached, as measured by the first tungsten mesh photodiode in the polarization analyzer. After the entire photon energy range had been scanned, the parameters were reset to the initial values, and the procedure repeated. Photoelectron spectra were taken at three kinetic energies 0.1, 0.5, and 1.0 eV, from just below the ionization threshold to approximately 22 eV photon energy.

In order to compare the CPE spectra taken at various kinetic energies, it was necessary to know the efficiency of the analyzing lens system as a function of electron energy. This was determined by measuring the analyzer transmission function using argon as a calibration gas, and comparing the observed count rates with accurately known cross sections.[37] This procedure enabled the three $E_k\neq0$ spectra to be normalized to each other, but not to the threshold spectrum. It was not feasible to compare the collection efficiency of the hemispherical analyzer with that of the threshold spectrometer. The collection efficiency of the hemispherical analyzer decreased with decreasing electron energy and therefore the statistics, and the degree of confidence in the collection efficiency normalization, were best for the 1.0 eV spectrum. All four spectra were corrected for the varying efficiency of the tungsten photodiode as a function of photon energy by using an accurately determined calibration curve.[38]

III. RESULTS

CPE spectra of acetylene at four different electron kinetic energies are shown in Fig. 1. The spectra are aligned so that the electron peaks due to direct photoionization occur at the same energy, i.e., on the binding energy scale, which is indicated at the top of the figure and is common to all four plots. The photon energy is also shown on each spectrum

The threshold electron spectrum ($E_k=0$) is similar to the conventional HeI(21.2 eV) photoelectron spectrum.[19,21] The dominant feature is the ground state (X), with the four lowest vibrational levels being observed. However, when the portion of the spectrum above 12 eV is examined closely, the contributions from the A and B states become discernible. In addition, a broad peak is observed between 13 and 14 eV photon energy, which remains stationary on the photon energy scale as E_k is varied.

The lower three frames of Fig. 1 show the $E_k\neq0$ spectra. Two observations are immediately apparent. Firstly, the remarkable decrease in the intensity of the X state with respect to the rest of the spectrum; and secondly, the significant contribution of electrons originating from states lying between approximately 12.5 eV and the threshold of the A state (16.36 eV). To facilitate the discussion of the spectra, we have partitioned it into four separate portions; the X, A, and B states, and the region between the X and A states, designated "Remainder." The relative intensities of these regions, calculated by summing the electron counts in each region, are plotted in Fig. 2. It should be noted that this representation overcomes the difficulty in the normalization of the threshold spectrum with the $E_k\neq0$ spectra.

The peaks due to electrons leaving the acetylene ion in the X, A, or B state, as a result of direct photoionization appear at a constant binding energy, and at a photon energy given by Eq. (1). In contrast to this, the peak previously mentioned as occurring between 13 and 14 eV photon energy, in the threshold spectrum,

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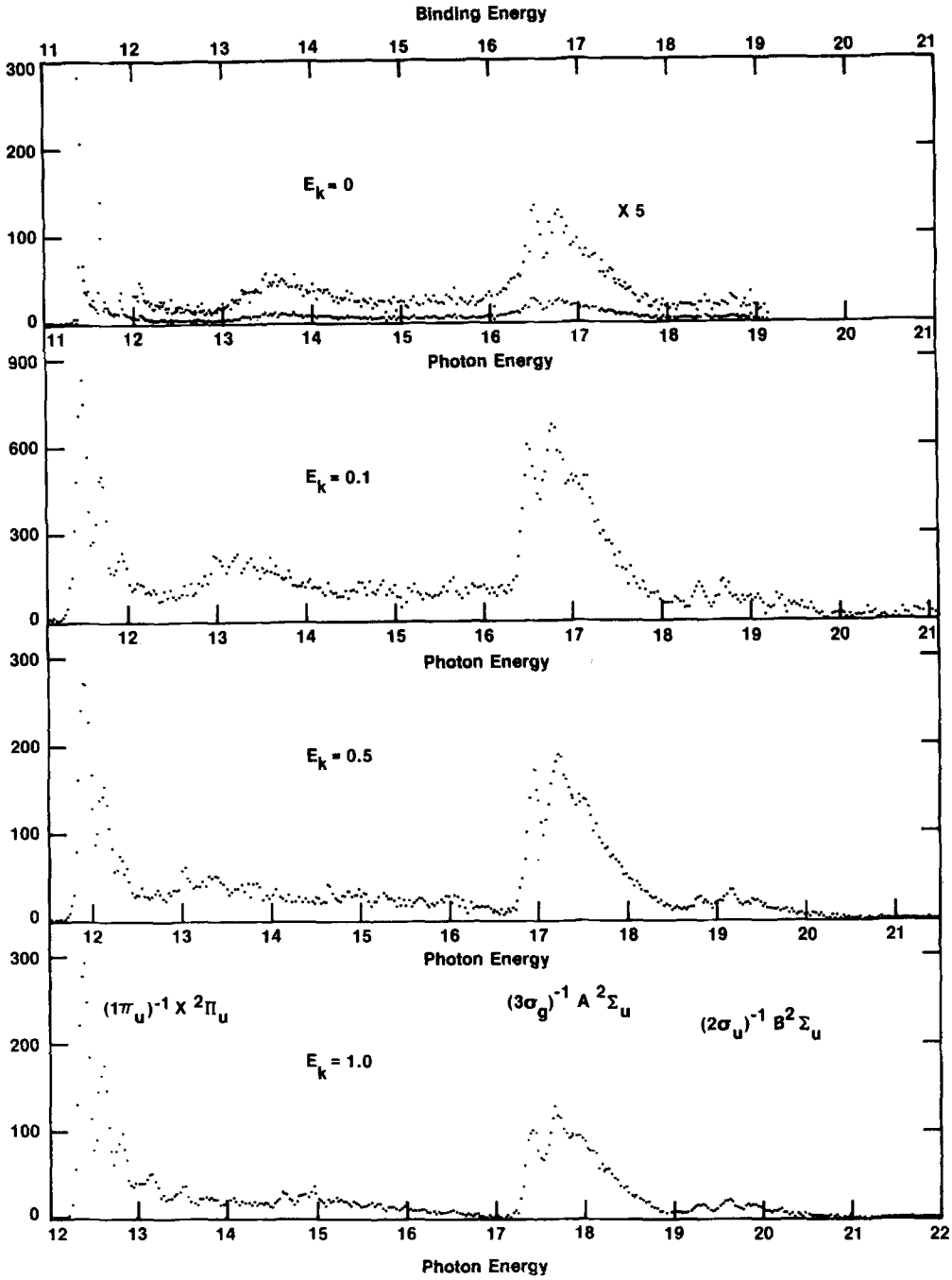

FIG. 1. Constant photoelectron energy spectra of acetylene at four electron kinetic energies; $E_k = 0, 0.1, 0.5$, and 1.0 eV. All spectra are aligned on a common binding energy $E_I = E_{ph} - E_k$ scale, shown at the top of the figure. The photon energy scale consequently shifts for each different E_k, and is indicated on the abscissa of each frame. The threshold electron spectrum $E_k = 0$ is plotted $\times 1$ and $\times 5$ above 12 eV.

continues to appear in approximately the same photon energy region as the electron energy is increased from zero. Such behavior is to be expected from an electron originating from an indirect process involving a transition to an excited state of the molecule which subsequently autoionizes. As the electron energy is increased, the collection efficiency and statistics are improved, and the broad peak show signs of having structure. At $E_k = 1$ eV structure becomes discernible with peak to peak splitting of approximately 0.4 eV. For $E_k = 1$ eV, the low energy portion of this autoionization structure probably lies within the X state band, and may account for the slightly enhanced $v = 2$ member. In addition, at $E_k = 0.5$ and 1.0 eV, a broad peak lying between 14.5 and 15.5 eV photon energy becomes noticeable, and again, shows some structure. At $E_k = 0$ and 0.1 eV, a contribution in this photon energy region is visible, but less easily distinguished from the general background level.

Finally, a comment should be made on the nonzero background intensity in the region between the X and A states. The experimental background level can be gauged from the electron intensity in the region below the ionization threshold, and can be seen to be negligible with respect to the intensity in the region being considered. Direct double ionization is a mechanism which produces electrons having a continuous distribution in energy. The double ionization threshold of acetylene is not known, but the corresponding threshold

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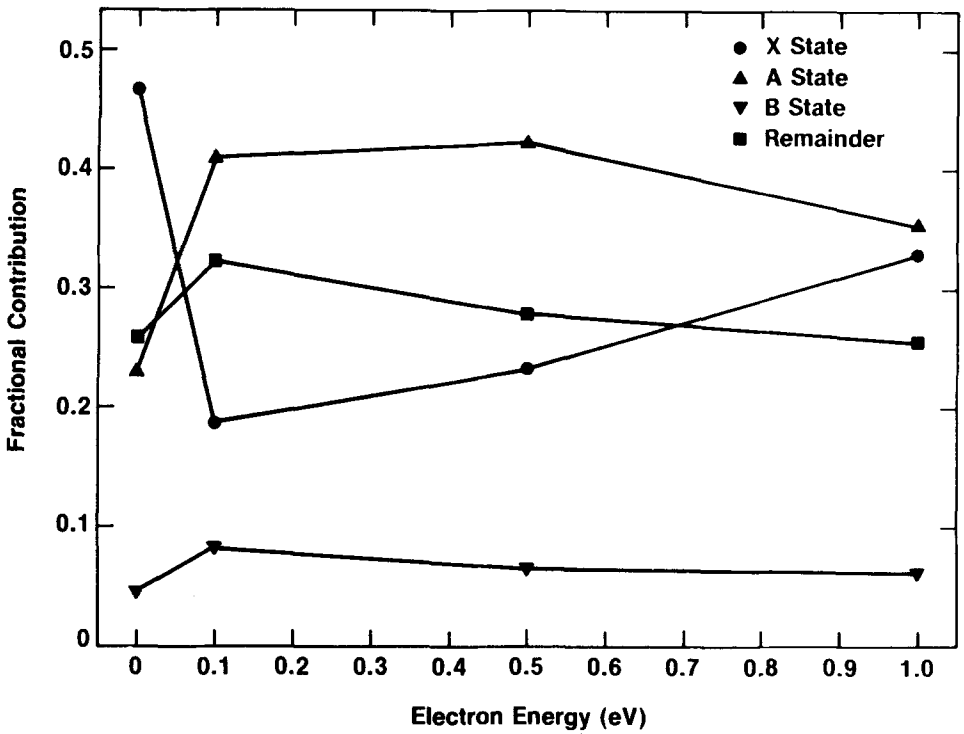

FIG. 2. The fractional contribution from various regions of the acetylene spectrum plotted as a function of electron energy.

for ethane occurs at 34.8 ± 0.8 eV.[39] If it is assumed that the threshold for acetylene also lies in the 30 to 40 eV range, then direct double ionization cannot be produced in the photon energy range covered in the present experiment. Hence, the continuous distribution of counts in the so called Franck–Condon gap, between the X and A states, indicates that this spectral region is spanned by neutral (valence and Rydberg) autoionizing states, which can decay with finite probability into excited vibrational levels of the X state such that photoelectrons are ejected with $0 \leq E_k \leq 1$ eV.

IV. DISCUSSION

The assignment of the main features appearing in the photoionization spectrum of acetylene,[11–17] and in particular, the two broad intense peaks around 13.3 and 15.3 eV, has been discussed recently.[16,23–26] As yet, no definitive picture has emerged although a number of points have been clarified. The chief purpose of this discussion is to see whether the present experimental study can shed any further light on the origin of the resonant structure lying between the ionization threshold and approximately 17 eV.

The first point that needs to be considered is whether it is possible to identify the neutral state giving rise to the prominent feature lying around 13 eV photon energy, and the channels available for autoionization. There is some controversy concerning the threshold value[15,16,40,41] for the onset of the first fragmentation process $C_2H_2 + h\nu \rightarrow C_2H^+ + H + e^-$. The most recent investigations[16,41] place the threshold at about 16.8 eV which means that any structure observed in the CPE spectra between the X and A states cannot result from any process involving fragmentation. Therefore, presumably, the excited neutral state is autoionizing into the ground ionic state. Recent calculations[16,23,26] have placed an excited neutral state lying at an energy between 13 and 14 eV with a width of approximately 1 eV. Hayaishi *et al.*[16] predicted a state lying at 13.9 eV with a theoretical oscillator strength of 0.1623, and assigned it to the transition $3\sigma_g \rightarrow 3\sigma_u$ (σ^*) converging to the second electronic state of the ion; $3\sigma_g^{-1}\,{}^2\Sigma_g$. Likewise, Langhoff *et al.*[23] and Machado *et al.*[26] have reported a $3\sigma_g \rightarrow 3p\sigma_u$ transition to a Rydberg state at $h\nu = 13.66$ eV with an oscillator strength of 0.1480. Therefore, it seems plausible that the feature appearing in all four CPE spectra between 12.5 and 14 eV photon energy results from the excitation $3\sigma_g \rightarrow 3\sigma_u$ ($3p\sigma_u$), followed by autoionization to the ground state. At this time, it is difficult to propose unambiguous assignments for the substructure occurring between 12.5 and 14 eV. Two conditions have to be satisfied simultaneously for such a peak to appear in a CPE spectrum. First, the photon energy must coincide with that required to cause a transition to a neutral excited state. Second, an autoionization transition must be allowed, between the excited neutral state and an ionic state, that yields an electron with the particular E_k value at which the energy analysis is being performed. When the energetically accessible region in the ionic state lies close to the origin, the number of available frequency modes becomes limited. This leads to a simplification of the autoionization process and may, to some extent, explain the increase in the structure observable between 12.5 and 14 eV as E_k increases from 0 to 1 eV. Thus, the present CPE spectra yield the interesting, though as yet unexplained, observation that the broad autoionization feature near $h\nu \simeq 13$ eV decays selectively to certain excited vibrational levels of the ground ionic state with the release of photoelectrons in the range $0 \leq E_k \leq 1.0$ eV. The prominence

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of substructure exhibiting peak to peak splitting of approximately 0.4 eV in the resulting CPE spectrum is a qualitative observation to be explained in future theoretical work. Note that earlier studies[24,25] of triply differential photoionization of acetylene focused on the region $E_{ph} \geq 13$ eV, $E_k > 0.8$ eV and thus omitted consideration of the weak autoionization-induced photocurrent with $E_k < 0.8$ eV. This observation serves to emphasize the complimentarity of the two approaches.

A second prominent feature appears in the photoionization spectrum between 15 and 16 eV, and it has been suggested that this is also due to autoionization. Calculations[16,23,26] place the transition $2\sigma_u \rightarrow 1\pi_g$, which converges onto the $2\sigma_u^{-1}\,{}^2\Sigma_u$ state of the ion, in this region. Hayaishi *et al.*[16] place it at 15.9 eV with an oscillator strength of 0.429, and Langhoff *et al.*[23] and Machado *et al.*[26] place it at 15.5 eV with an oscillator strength of 0.8036. The large oscillator strength and the absence of significant Rydberg structure in the same channel has led to the suggestion[25] that the excited state is shape resonantly enhanced. While the calculated transition energies do not reproduce the spectral location of the $2\sigma_u \rightarrow 1\pi_g$ transition very accurately, it is likely that this intense, broad autoionizing feature is responsible for the peak in the photoionization spectrum at $h\nu \simeq 15.3$ eV. Furthermore, as this strong autoionization peak dominates the total photoionization spectrum in this photon energy region, it appears plausible to correlate the weak, but real, electron yield in the CPE spectrum between 14.5 and 15.5 eV with this peak. The weak intensity of this structure in the CPE spectrum is at first surprising, since Suzuki and Maeda[42] have reported that the contribution from autoionization to the total ion intensity exceeds 35% near $h\nu = 16$ eV. However, this suggests that the decay of the intense autoionizing state near $h\nu = 15.3$ eV has a low and decreasing branching ratio for photoelectrons between $E_k = 1.0$ eV and $E_k = 0$ eV. This observation is another piece of evidence to guide future studies on the dynamics of autoionization in acetylene in this spectral range.

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