Photon Energy Dependence of the $1\sigma_u/1\sigma_g$ Intensity Ratio in Carbon 1*s* Photoelectron Spectroscopy of Ethyne

T. D. Thomas,[1] N. Berrah,[2] J. Bozek,[3] T. X. Carroll,[4] J. Hahne,[1] T. Karlsen,[5] E. Kukk,[2,3] and L. J. Sæthre[5]
[1]*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003*
[2]*Physics Department, Western Michigan University, Kalamazoo, Michigan 49008*
[3]*Advanced Light Source, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720*
[4]*Keuka College, Keuka Park, New York 14478*
[5]*Department of Chemistry, University of Bergen, N-5007 Bergen, Norway*
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High-resolution measurements of the C 1*s* photoelectron spectrum of ethyne (acetylene) at photon energies between 297 and 348 eV have been analyzed to give the energy dependence of the relative cross sections for ionization of the $1\sigma_g$ and $1\sigma_u$ orbitals. The $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio is greater than 1 at the lowest photon energies but reaches a minimum of about 0.6 between 315 and 320 eV. These results can be understood in terms of the effect of shape resonance on the ionization cross section and provide quantitative information on the position and magnitude of such resonances. [S0031-9007(98)08336-7]

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Shape resonances in the core excitation of small molecules have been of considerable interest, especially in light of the suggestion that the position of the resonance above threshold is related to the size of the molecule and, thus, could be used as a ruler to measure molecular dimensions [1]. Subsequent discussion has raised questions about the criteria for establishing that a particular structure in a photoabsorption spectrum is a shape resonance [2]. Kempgens *et al.* have recently concluded that in ethane and ethene there are no readily identifiable shape resonances, and that in ethyne (acetylene) there is only a weak, broad feature at a photon energy of about 312 eV that may be a shape resonance [3]. These observations are important in that these are key molecules in establishing the relationship between bond length and position of the resonance. We present here new experimental results that allow us to decompose the cross sections for ethyne reported by Kempgens *et al.* into contributions from $1\sigma_g$ ionization and $1\sigma_u$ ionization. Because of the dipole selection rule, the former is assumed to be associated with outgoing electrons of *u* character and the latter with outgoing electrons of *g* character. The feature seen by Kempgens *et al.* is found to be in a region of high relative probability for $1\sigma_g$ ionization, as would be expected for a σ_u shape resonance. Our results, therefore, lend support to their tentative identification of this feature with the shape resonance. The position of maximum cross section for ionization into the *u* exit channel is at a photon energy of about 310 eV. This is the same as the value of 310 eV proposed by Hitchcock *et al.* [1] for the position of the sigma shape resonance and significantly higher than the value of about 304 eV that has been predicted theoretically [4].

These experimental results also provide a test of theoretical calculations of the photoionization cross section near threshold [4,5] in both the *u* and *g* exit channels. The comparison shows qualitative but not quantitative agreement.

Kempgens *et al.* have recently shown that the carbon 1*s* photoelectron spectrum of HCCH has a splitting between the $1\sigma_u^{-1}$ and $1\sigma_g^{-1}$ states of 105 meV [6]. This large splitting, which is in agreement with theoretical predictions, arises because of the very short bond length of the carbon-carbon triple bond and consequent enhanced overlap of the 1*s* wave functions. Confirming measurements for HCCH and DCCD have been reported by Thomas *et al.* [7]. Using photons from the Advanced Light Source, we have measured this spectrum at photon energies between 297 and 348 eV. For most of these measurements the resolution is significantly narrower than the natural line width of the carbon 1*s* hole, and this high resolution has allowed us to see features of the photoelectron spectrum that are not readily apparent in the previous results and to gain new insight into the shape resonance.

For photon energies of 300 eV and less, the cross section for the ionization of the $1\sigma_u$ molecular orbital is greater than that for ionization of the $1\sigma_g$ orbital [3]. Our results show that the ratio of the cross sections $(1\sigma_u^{-1}/1\sigma_g^{-1})$ decreases as the photon energy increases and goes through a minimum of about 0.6 at a photon energy of about 317 eV. This energy corresponds roughly to the maximum in what may be the σ_u shape resonance in ethyne [3]. The energy dependence of the ratio can be used to partition the measured cross section for 1σ ionization in HCCH [3] into contributions from the $1\sigma_u^{-1}$ and $1\sigma_g^{-1}$ channels. The $1\sigma_g$ ionization is due primarily to dipole excitation of core electrons to the virtual molecular orbitals of *u* character that give rise to the shape resonance, and thus provides important information about this resonance.

The measurements were made on the high-resolution atomic, molecular, and optical physics beam lines (9.0.1 and 10.0.1) of the Advanced Light Source with a Scienta

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SES-200 electron spectrometer. Three sets of measurements were made. In the first, HCCH and DCCD were studied at a photon energy of 330 eV and at an angle of 54.7° with respect to the polarization direction of the photons. In this set of measurements, particular care was taken to characterize the resolution of both the monochromator and the electron spectrometer. For the monochromator, measurements of the photon absorption by CO near the π resonance were fit with Voigt functions at several different pressures. The Lorentzian component (due to the natural linewidth of the carbon 1*s* hole) was found to be in satisfactory agreement with the value of 85 meV reported by others [8], and the Gaussian component, which we attribute to the monochromator resolution, was 32 meV. The electron-spectrometer resolution function was determined to be nearly Gaussian with a full width at half maximum of 28 meV through measurements of the Xe 5*s* photoelectron spectrum. The combined experimental resolution is thus about 42 meV. In the second set of experiments the photoelectron spectrum of HCCH was measured at several photon energies between 310 and 340 eV at an angle of 0° with respect to the photon polarization. The slits on the monochromator and electron spectrometer were chosen from the design parameters to give a total resolution of 50 meV. The third set of measurements, which were undertaken to extend the energy and angular range of our measurements, were the first experiments of this type on line 10.0.1. Since not all facilities were in place, it was not possible to completely characterize the beam line and the spectrometer. The overall resolution was estimated from simultaneous measurements of the argon 2*p* photoelectron spectrum and ranged from 65 to 75 meV, for measurements at 0° to the photon polarization, to 95 to 103 meV, at 54.7°, and 132 meV, at 90°. The reason for this variation of resolution with angle is not known, but it does not significantly affect our analysis.

The carbon 1*s* spectrum measured for HCCH in the first set of experiments (photon energy of 330 eV and an angle of 54.7°) is shown in Fig. 1. The data for DCCD are similar but show a distinct peak just above 291 eV because of contributions from CD stretching modes [7]. The principal peak is due to the transition to the vibrational ground state of the ion. The most prominent part results from ionization of the $1\sigma_g$ orbital and the shoulder at lower ionization energy from the $1\sigma_u$ orbital. It is apparent that the cross section for $1\sigma_u$ ionization is less than that for $1\sigma_g$. The *u*-*g* split shoulder on the high-energy side of the main peak arises from the $v = 1$ excitation of the carbon-carbon stretching mode. The solid curve shows a fit to the data. For this we have assumed that each peak in the spectrum has the shape given by convolution of a Gaussian resolution function with a shape given by the theory of van der Straten *et al.* [9] to account for the interaction between the photoelectron and the Auger electron. For the spectrum shown in Fig. 1, we have used a lifetime width of 105 meV, which is close to the value that

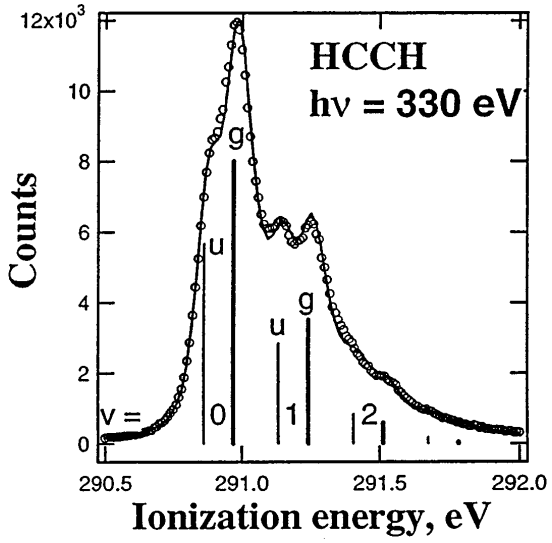

FIG. 1. Carbon 1*s* photoelectron spectrum of HCCH at a photon energy of 330 eV. The points represent the data and the solid curve a fit assuming that carbon-carbon stretching is the only mode contributing to the vibrational structure. The data and the fit extend to both higher and lower energies than shown here. The vertical bars indicate the position and intensity of the different vibrational transitions. The light lines are for $1\sigma_u^{-1}$, and the heavy lines are for $1\sigma_g^{-1}$. The intensities shown for $v = 2$ and $v = 3$ contain contributions from CH stretching modes, which were not considered in the fitting procedure.

gives the best fit. For the vibrational structure, we have considered only the carbon-carbon stretching mode, since theoretical calculations [7] indicate only weak excitation of the carbon-hydrogen stretching modes (and no excitation of other modes). In any event, the carbon-hydrogen stretching modes are found only above the energy of the $v = 1$ peaks for the carbon-carbon stretching modes. The adjustable parameters in the fit are the vibrational spacing, the *u*-*g* spacing, the intensities of 8 peaks ($v = 0$ to 3 for the CC stretching mode of $1\sigma_g$ and for $1\sigma_u$), a constant background, and the position of the $1\sigma_u$, $v = 0$ peak. Because no contributions from the CH stretching modes have been included in the fitting procedure, the intensities found for $v = 2$ and $v = 3$ are of limited significance. The *u*-*g* splitting and vibrational frequency obtained from this fit are in agreement with those previously reported by Kempgens *et al.* [6]. For present purposes, the relevant parameter is the $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio for the $v = 0$ peak, which, for the data shown here, is 0.71. The results at an angle of 0° are essentially the same. In fitting the DCCD data, we have confined the fit to the $v = 0$ peak, since theory predicts and the data indicate noticeable contributions from carbon-deuterium stretching modes to the shoulder on the high-energy side of the main peak. In this case, the fitting parameters are the heights and positions of the two $v = 0$ peaks and the background. The $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio is 0.74. The other spectra were fit in the manner described for HCCH.

For photon energies above 300 eV there is no strong evidence for an angular dependence of the $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio. At 300 eV, this ratio is greater than 1 (as noted by Kempgens *et al.* [3]) and is considerably higher at 54.7° than at 0°. At this energy, there are thought to be significant contributions from two-hole, two-electron excited states that decay to the one-hole ionized state, and it is possible that this mechanism affects the angular distribution. Also, above 300 eV there is no strong evidence to indicate a variation of the vibrational profile with photon energy. There is, however, an indication from the $v = 1/v = 0$ intensity ratios that there is slightly less vibrational excitation for $1\sigma_g$ ionization than for $1\sigma_u$ above 300 eV. The difference is small and does not have a significant effect on our subsequent analysis of these results.

The photon-energy dependence of the $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio for $v = 0$ is shown in Fig. 2(a). The uncertainties indicated are those given by the fitting procedure; on the basis of the scatter of the data, we estimate an actual uncertainty of about 0.05 for a typical measurement. Data at 317 eV for both HCCH and DCCD are from Ref. [7]. In this case the fitting was done with a theoretical prediction of the vibrational structure, as outlined in Ref. [7], but with the $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio as a fitting parameter. From Fig. 2(a), it is apparent that the experimental value of this ratio goes through a minimum between 315 and 320 eV.

The position of the minimum seen in Fig. 2(a) corresponds approximately to a region of high cross section for single-hole [10] ionization of the carbon 1*s* electrons from ethyne, as reported by Kempgens *et al.* [3], and shown as the open circles in Fig. 2(b). These authors have suggested that if there is a shape resonance in ethyne, it is in the region near 312 eV. In N_2, which is isoelectronic with ethyne, x-ray emission spectroscopy [11] indicates that the σ resonance has *u* character. If this is also the case for ethyne, then the resonance provides a mechanism for enhanced emission to the $1\sigma_g^{-1}$ final state. For emission through the σ_u resonance only electrons in the $1\sigma_g$ orbital can participate, since excitation of an electron from $1\sigma_u$ to $k\sigma_u$ would be forbidden by the dipole selection rule.

We have used our measurements of the $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio to decompose the single-hole ionization cross section into contributions from $1\sigma_u$ and $1\sigma_g$ ionization. These are shown as the open ($1\sigma_u$) and closed ($1\sigma_g$) triangles in Fig. 2(b). The two heavy lines show the predictions of Farren *et al.* for these partial cross sections [4,5], and the two light lines are smooth curves through the data to show more clearly the overall trend. Both theory and experiment show a monotonically decreasing cross section with increasing energy for $1\sigma_u$ ionization and a peak in the cross section for $1\sigma_g$ ionization. Quantitatively, the predicted cross sections are higher than measured and the peak in the cross section for $1\sigma_g$ ionization is predicted to be at a lower energy than it is observed to be. However,

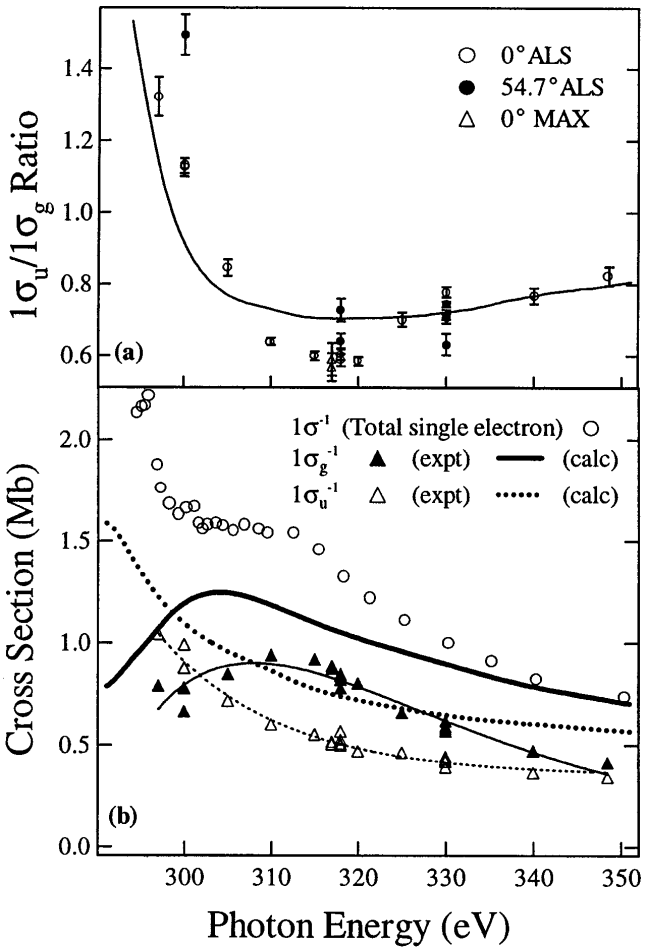

FIG. 2. (a) The ratio of the cross sections for ionization of the $1\sigma_u$ and $1\sigma_g$ electrons of ethyne as a function of photon energy. The open circles represent 0° results for HCCH. The closed circles show 54.7° results for both HCCH and DCCD. The triangles are derived from 0° data for HCCH and DCCD from Ref. [7]. The solid line shows a theoretical calculation from results given in Ref. [5]. (b) Cross section for carbon 1*s* ionization in HCCH. Open circles represent the total single-hole cross section, from Ref. [3]. Triangles show the cross section for ionization of $1\sigma_u$ (open) and $1\sigma_g$ (closed). The heavy solid lines show theoretical results from Ref. [5], and the light lines are smooth curves drawn to show the overall trends more clearly.

it is to be noted that the experimental cross sections include only one-electron excitations, whereas the calculated cross sections include contributions from other ionization processes, such as valence excitations accompanying core ionization. The difference in magnitude between calculation and experiment is, therefore, in the expected direction.

From the calculated cross section [5], we can also obtain a predicted $1\sigma_u^{-1}/1\sigma_g^{-1}$ intensity ratio, which is shown as the solid line in Fig. 2(a). We see that the theory reproduces the trend of the data, indicating that most of the basic physics has been included.

The closed triangles represent an upper bound to the cross section from the σ_u resonance, since there may be

contributions from other channels. Farren's calculations [5] indeed show emission into a π_u exit channel with a peak in the cross section at the same energy and of the same magnitude as predicted for the σ_u exit channel. Most of the high-energy tail in the predicted cross section is due to the π_u channel.

A prominent feature in the photon absorption spectrum at about 310 eV was assigned by Hitchcock *et al.* [1] to the shape resonance. Kempgens *et al.* [3] have concluded that this feature is due primarily to excitation of two-hole, one-particle states in the ionization process, and that a much weaker feature in the single-hole ionization cross section is a possible, though not certain, candidate for the expected resonance. Our measurements have made it possible to decompose their measurements of the total one-hole cross section into components corresponding to $1\sigma_g$ and $1\sigma_u$ ionization. The former, which contains contributions from ionization through the σ_u resonance, shows a maximum also at about 310 eV, and, thus, supports the assignment of a σ_u resonance in this energy region. However, the calculations by Farren [5] indicate that there is also a significant contribution from excitation to a π_u exit channel to this cross section. Thus, although the evidence supports the assignment of a σ_u shape resonance at about 310 eV, it also makes clear, as Kempgens *et al.* [3] have noted, that the assignment of this resonance requires more information than is available in a total cross section measurement.

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