

High-Resolution Carbon 1s Photoelectron Spectrum of Small Molecules

N. Berrah¹, K.J. Børve², J. Bozek³, T. X. Carroll⁴, J. Hahn⁵, E. Kukk^{1,3}, L. J. Sæthre², and T. D. Thomas⁵

¹Physics Department, Western Michigan University, Kalamazoo, MI 49008

²Department of Chemistry, University of Bergen, N-5007 Bergen, Norway.

³Advanced Light Source, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720

⁴Keuka College, Keuka Park, NY 14478

⁵Oregon State University, Corvallis, OR 97331-4003

INTRODUCTION

A challenge for inner-shell photoelectron spectroscopy has been the study of organic molecules in which the carbon atoms have similar ionization energies even though they are quite distinct chemically. Only recently has it been possible to resolve the contributions from these carbons in the carbon 1s photoelectron spectrum of this molecule and to correlate the ionization energies with the reactivity.[1] The very high resolution capabilities of the Advanced Light Source present a long-awaited opportunity to examine inner-shell photoelectron spectra of such molecules and to gain chemical insights that were previously inaccessible.

The complete analysis of such a spectrum requires an understanding of a number of factors: the vibrational excitation that occurs during ionization, the line broadening that results from the finite lifetime of the core-ionized state, and the distortion of the line shape that results from interaction of the outgoing photoelectron with the Auger electron (emitted in the deexcitation of the core hole). In addition it is necessary to understand the instrumental features that affect the spectrum. These include the calibration of the energy scales of the monochromator and electron-energy analyzer, the resolution of the photon beam, the resolution of the electron-energy analyzer, and the variation of the analyzer transmission with electron energy.

Our program during 1998 aimed at providing a basis for this understanding with extension of our earlier work on CH₄, CO, CO₂, CF₄, and H₂C=CH₂ to include HCCH, CH₃CH₃, CH₃C≡CH, CF₃C≡CH, CH₃C≡CCH₃, CF₃C≡CCF₃, CF₃CH₂CH₃, and H₂C=C=CH₂. Although analysis is still in progress for much of the data, interesting results have been obtained for ethyne (HCCH), propyne (CH₃C≡CH) and methane (CH₄). These are summarized below.

CARBON 1s PHOTOELECTRON SPECTRUM OF ETHYNE [2]

When core-ionization takes place in a molecule, there is typically vibrational excitation of the resulting ion, leading to vibrational structure in the photoelectron spectrum. The carbon 1s ionization spectrum of ethyne shows additional structure because there are two closely spaced molecular orbitals (1σ_g and 1σ_u) resulting from combination of the equivalent atomic carbon 1s orbitals. This effect can be seen in the spectrum shown in Fig. 1, measured using the high-resolution beamline for atomic and molecular physics. In this spectrum the principal peak is due to the transition to the vibrational ground state of the ion. The most prominent part of this peak results from

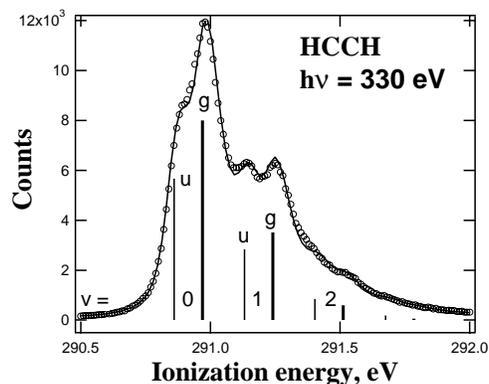


Figure 1. Carbon 1s photoelectron spectrum of HCCH

ionization of the $1\sigma_g$ orbital and the shoulder at lower ionization energy from the $1\sigma_u$ orbital. The u-g split shoulder on the high-energy side of the peak results from the $v = 1$ excitation of the carbon-carbon stretching mode. It is apparent that the cross section for $1\sigma_u$ ionization is less than that for $1\sigma_g$ ionization.

That the intensities for these two ionizations are not the same is related to the existence of a σ_u shape resonance in the photon energy range studied here, and is of especial interest because of on-going discussion of the criteria for identifying such shape resonances. In the spectrum shown in Fig.1 the intensity for $1\sigma_g$ ionization is enhanced, since the transition $1\sigma_g \rightarrow k\sigma_u$ is allowed by dipole selection rules but the transition $1\sigma_u \rightarrow k\sigma_u$ is not. We have mapped out the ionization intensity ratio ($1\sigma_u/1\sigma_g$) as a function of photon energy, and these results are shown in Fig. 2a. Combining these with measurements of the carbon 1s ionization cross section [3], we obtain cross sections for the ionization of the $1\sigma_g$ and $1\sigma_u$ orbitals. These are shown in Fig. 2b, where they are compared with theoretical predictions of the cross sections [4]. Both theory and experiment show a cross section for $1\sigma_u$ ionization that decreases monotonically with increasing photon energy and a cross section for $1\sigma_g$ ionization that has a peak. The theoretical ionization intensity ratio ($1\sigma_u/1\sigma_g$), shown as the solid curve of Fig. 2a, reproduces the trend of the data. Although there is not quantitative agreement between theory and experiment, it is apparent that the theory includes most of the basic physics of the process.

These results support the assignment of a σ_u shape resonance at a photon energy of about 310 eV; they also make clear the importance of having detailed information for making such an assignment.

CARBON 1s PHOTOELECTRON SPECTRUM OF METHANE [5]

Carbon 1s photoelectron spectra have been measured for CH_4 at photon energies of 302, 320, and 330 eV and for CD_4 at 330 eV with an instrumental resolution about half the natural line width. The spectrum of CH_4 at 330 eV is shown in Fig. 3. The spectra have been analyzed to obtain vibrational spacings, vibrational intensities, and the lifetime of the carbon 1s core hole state. The vibrational intensities vary with photon energy, in

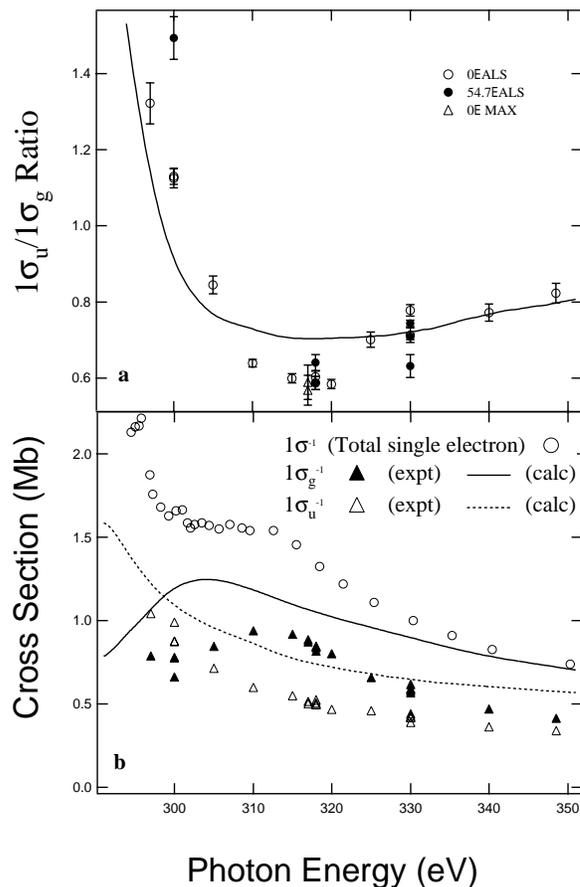


Figure 2. a. The ratio of the cross sections for ionization of the $1\sigma_u$ and $1\sigma_g$ orbitals in ethyne. b. Cross section for carbon 1s ionization in HCCH. Circles: total single-hole cross section. Triangles: cross section for ionization of $1\sigma_u$ (open) and $1\sigma_g$ (closed). Lines are theoretical cross sections for ionization of $1\sigma_u$ (dashed) and $1\sigma_g$ (solid).

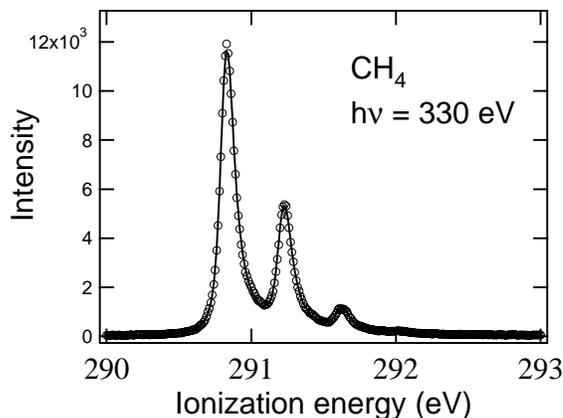


Figure 3. Carbon 1s photoelectron spectrum of CH_4

agreement with earlier results [6]. At 330 eV, the observed vibrational intensities for both CH_4 and CD_4 can be understood only if anharmonic effects (consistent with the predictions of theory) are included. On the other hand, the vibrational spacings in CH_4 show no evidence for anharmonicity (in contrast with theoretical predictions). In CD_4 the observed anharmonicity in the vibrational energy spacings is about half of the predicted value, but the experimental and theoretical values differ only by an amount comparable to the experimental uncertainty. The measured values of the lifetime show a dependence on photon energy; this is attributed to failure of the theory of post-collision interaction to predict correctly the observed electron spectrum near threshold. At 330 eV, the measured Lorentzian lifetime, 93-95 meV, agrees with predictions of simple theory, but not with the prediction of more complete theory. It is also observed that there are systematic discrepancies between the observed line shapes and those predicted by the theory of post-collision interaction.

CARBON 1s PHOTOELECTRON SPECTRUM OF PROPYNE [7]

In propyne, $\text{CH}_3\text{C}\equiv\text{CH}$, the three carbons are chemically inequivalent. The $\text{CH}\equiv$ unit is the site for electrophilic attack and is the basic end of the molecule. The central carbon, while susceptible to attack is not so reactive as the $\text{CH}\equiv$ carbon. The CH_3 carbon, less reactive than the others, is the acidic end of the molecule. The inner-shell photoelectron spectroscopy of this molecule provides a basis for a better understanding of its chemistry, and, by extension, that of more complex molecules. Such knowledge can enhance our ability to predict properties of molecules and to design molecules with particular properties.

Measurements of the carbon 1s photoelectron spectrum of propyne by Cavell showed only a single asymmetric peak. Although he analyzed this in terms of three components, each representing a contribution from one of the carbon atoms, Cavell expressed reservations about both the positions and the assignments of each component. It was, therefore, difficult to draw firm conclusions about the chemistry of the molecule from these measurements.

With the high-resolution capabilities of the Advanced Light Source, it has been possible to resolve the contributions from the three inequivalent carbons in propyne. The spectrum for this molecule is shown in Fig. 4, where it is compared with that of ethyne (above) and ethane (below). Shown as a dashed line in the center spectrum is a representation of the earlier spectrum measured by Cavell. The additional structure that is revealed at higher resolution is striking.

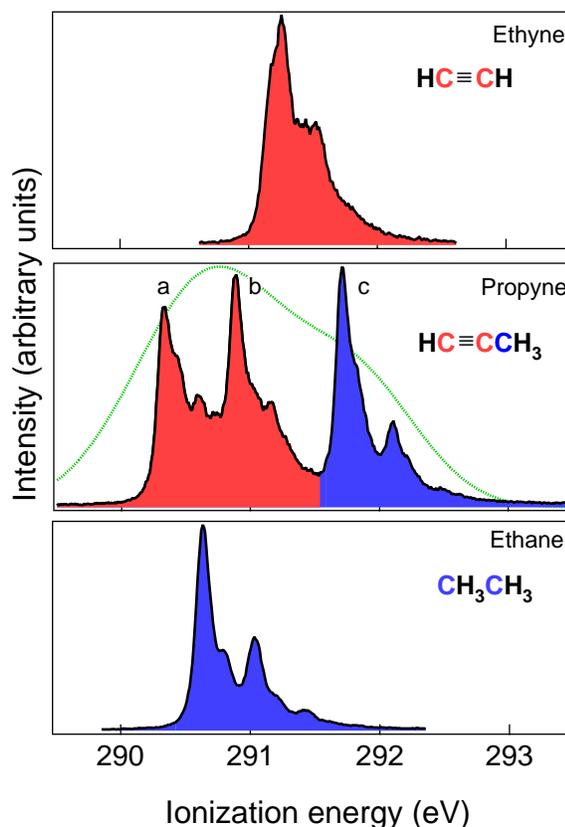


Figure 4. carbon 1s photoelectron spectra of ethyne, propyne, and ethane

The three peaks in the propyne spectrum can be assigned to the three carbons by comparison with the model spectra of ethyne and ethane. Comparison with the spectrum of ethane shows a strong resemblance between the peak labeled "c" in propyne and the ethane spectrum, and we are therefore confident in assigning this peak to the CH₃ group in propyne. The vibrational pattern of peaks "a" and "b" are similar to the structure observed for ethyne, allowing us to assign these two peaks to the acetylenic part of the molecule. These assignments are in accord with theoretical calculations of both their shapes and positions, and these calculations allow us to assign peak "a" to the CH carbon and peak "b" to the central carbon of propyne.

The results shown here for propyne indicate that, with the high-resolution capabilities now available, the techniques of x-ray photoelectron spectroscopy can be extended into studies of hydrocarbons. A richness of detail is observed, both in vibrational structure and in the variation in ionization energy. The former provides an important test of ab initio theory and the latter provides insight into a variety of fundamental chemical phenomena.

REFERENCES

1. L. J. Sæthre, O. Sværen, S. Svensson, S. Osborne, T. D. Thomas, J. Jauhiainen, and S. Aksela, *Phys. Rev. A* **55**, 2748 (1997). L. J. Sæthre, T. D. Thomas, S. Svensson. *J. Chem. Soc. Perkin Trans. 2*, 749 (1997).
2. T. D. Thomas, N. Berrah, J. Bozek, T. X. Carroll, J. Hahne, T. Karlsen, E. Kukk, and L. J. Sæthre, *Phys. Rev. Lett.* **82**, 1120 (1999).
3. B. Kempgens *et al.*, *Phys. Rev. Lett.* **79**, 35 (1997); *J. Chem. Phys.* **107**, 4219 (1997).
4. R. E. Farren, J. A. Sheehy, and P.W. Langhoff, *Chem. Phys. Lett.* **177**, 307 (1991). R. E. Farren, Ph. D. thesis, Indiana University, Bloomington (1989).
5. T. X. Carroll, N. Berrah, J. Bozek, J. Hahne, E. Kukk, L. J. Sæthre, and T. D. Thomas, *Phys. Rev. A*, in press.
6. H. M. Köppe, B. S. Itchkawitz, A. L. D. Kilcoyne, J. Feldhaus, B. Kempgens, A. Kivimäki, M. Neeb, and A. M. Bradshaw, *Phys. Rev. A* **53**, 4120 (1996).
7. L. J. Sæthre, N. Berrah, J. D. Bozek, K. J. Børve, T. X. Carroll, E. Kukk, and T. D. Thomas, submitted to *Science*.

This work was supported by the National Science Foundation under Grant No. CHE-9727471, by the Division of Chemical and Material Sciences, Office of Energy Research, of the U. S. Department of Energy, and by the Research Council of Norway (NFR).

Principal investigator: T. Darrah Thomas, Department of Chemistry, Oregon State University. Email: thomast@chem.orst.edu. Telephone: 541-737-6711.