

# Inner-Shell Photoelectron Spectroscopy of Atoms and Small Molecules

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## INTRODUCTION

High-resolution inner-shell photoelectron spectra of molecules reveal a number of features that relate to the chemistry of the molecule and to the chemical physics and dynamics of the ionization process. Among these are chemical shifts of the ionization energy, vibrational excitation, lifetime broadening, distortion of the line shape resulting from interaction of the outgoing photoelectron with the Auger electron (emitted in the deexcitation of the core hole), localization-delocalization effects in molecules with equivalent atoms, and, for ionization of levels with  $l > 0$ , molecular-field splitting, which removes the degeneracy of levels with  $j \geq 3/2$ . Our work during the last several years has aimed at using the high-resolution capabilities of the Advanced Light Source to provide new information on all of these features.

During 2000 our efforts were focused on analyzing the spectra taken at the ALS in previous years and on new experiments to extend our earlier studies. The year saw the publication of our work on the carbon 1s linewidth in carbon dioxide<sup>1</sup> (described in last year's report) and publication of a paper on the vibronic structure seen in the core ionization of ethyne<sup>2</sup> (described below). Brief reports of some of our recent results were presented at a number of meetings.<sup>3</sup> One master's thesis completed in 2000 was based in part on results obtained at the ALS.<sup>4</sup>

New experiments have been concerned especially with investigations where the very-high resolution capabilities of the Advanced Light Source open up new opportunities to investigate the features described above. Examples of this work are described below. In addition, we have done experiments to provide accurate measurements of inner-shell ionization energies<sup>4</sup> and studies of the effect of post-collision interaction (PCI) on the shape of a line in the photoelectron spectrum.

## VIBRONIC EXCITATION IN THE CARBON 1s PHOTOELECTRON SPECTRUM OF ETHYNE, ETHENE, AND ETHANE

The molecules ethyne ( $\text{HC}\equiv\text{CH}$ ), ethene ( $\text{CH}_2=\text{CH}_2$ ), and ethane ( $\text{CH}_3\text{CH}_3$ ) each have two equivalent carbons. As a result there are two carbon 1s ionization energies for each molecule, resulting from the bonding ( $1\sigma_g$ ) and antibonding ( $1\sigma_u$ ) combinations of the carbon 1s atomic orbitals. In ethyne, with a short triple bond between the carbons, the splitting between these orbitals is relatively large,  $\sim 100$  meV, whereas for ethane, with a long single bond, it is expected to be small. Ethene is intermediate between these two. If the splitting is *very* large, then only symmetric vibrational modes are expected in the carbon 1s photoelectron spectrum; if the splitting is small, then coupling is possible between vibronic states of the  $1\sigma_g$  core-hole electronic state and those of the  $1\sigma_u$  state. This vibronic coupling leads to the possibility that non symmetric modes will be excited during core-

ionization. However, in the limit of very strong vibronic coupling, no splitting will be observed between the  $1\sigma_g$  and  $1\sigma_u$  core-hole states. Ethyne is at neither extreme. The  $1\sigma_g$  -  $1\sigma_u$  splitting is apparent in the spectra for  $\text{HC}\equiv\text{CH}$  and  $\text{DC}\equiv\text{CD}$  that we have measured at the ALS, but so also is the excitation of the antisymmetric carbon-hydrogen stretching mode. With a suitable development of the theory of vibronic coupling we have been able to account quantitatively for the experimental spectra, obtaining structural parameters that are in good agreement with those predicted by *ab initio* theory.<sup>2</sup>

In ethane and ethene the bond lengths are longer than in ethyne, and the splitting between the *gerade* and *ungerade* states is correspondingly smaller. It is of interest to determine whether the splitting is large enough to have an observable effect on the spectrum, and, towards that end, during 2000 we measured carbon 1s spectra for  $\text{CH}_3\text{CH}_3$ ,  $\text{CD}_3\text{CD}_3$ ,  $\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CD}_2$ , *cis*-CHDCHD, and *trans*-CHDCHD. The deuterated isotopomers are included because our experience with HCCH and DCCD indicates that these provide us with independent information in establishing the vibrational parameters and the dynamics of the vibrational excitation. We have further extended the theory of vibronic coupling so that it can deal with the more complicated vibrational excitation that is found in these molecules (compared with ethyne). Analysis of these results is in progress.

### THE CORE-HOLE LINE SHAPE

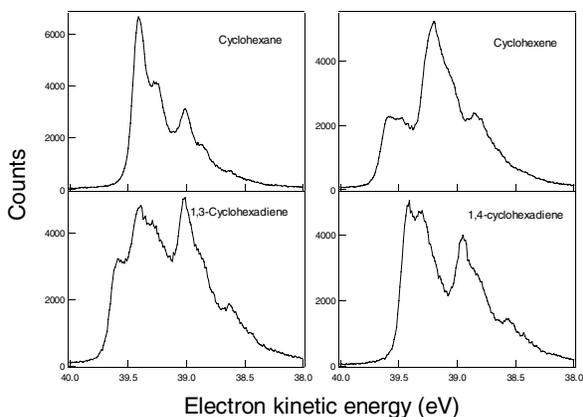
Well above threshold, the line shape for an inner-shell photoelectron line is expected to be Lorentzian, with the Lorentzian linewidth,  $\Gamma$ , related to the lifetime of the core hole,  $\tau$ , through the relationship  $\Gamma\tau=\hbar$ . Typical linewidths for carbon 1s holes are  $\sim 100$  meV. Near threshold, the effect of lifetime on the linewidth and shape is amplified by the interaction of the low-energy photoelectron with the Auger electron that is emitted in the deexcitation process. One of our projects during 2000 has been to investigate the question of how well does existing theory<sup>5</sup> describe this line shape. Towards that end, we have measured the argon 2p photoelectron and LMM Auger spectrum at several photon energies near threshold and well above threshold. We find that the theory (when convoluted with a Gaussian function to represent the experimental resolution) gives an excellent fit to the data. However, the parameters (linewidth and resolution) derived from this procedure are not self-consistent and do not agree well with those obtained from other experiments. On the other hand, if we fix the resolution at the values measured independently, then the linewidths are consistent, but the agreement between the theoretical and experimental line shapes is less good. We will continue the analysis of these results in the year ahead.

### CALIBRATION OF THE ENERGY SCALE FOR PHOTOELECTRON SPECTRA

Our experience with synchrotron radiation is that the absolute energy scales for both the photons and the electron-energy analyzer are unreliable. As a result, it is important to have an internal calibration when accurate energies are needed. Towards that end, we have measured the carbon 1s photoelectron spectra for a number of molecules in a mixture with argon. The known argon  $2p_{3/2}$  photoelectron ionization energy provides an internal standard, and these measurements will provide additional potential standards for such measurements. This work forms part of the MS thesis of Velaug Myrseth.<sup>4</sup>

## CHEMICAL EFFECTS ON CARBON 1s IONIZATION ENERGIES

A particular concern of ours has been to use the high-resolution capability of the ALS to study carbon 1s photoelectron spectra in hydrocarbons. A typical example is propyne ( $\text{HC}\equiv\text{CCH}_3$ ), which was described in our 1998 report. In this molecule the three carbons have very different chemical properties but similar ionization energies. The facilities at the ALS have made it possible for us to get a detailed understanding of this and related molecules. A more recent example showing the power of the facility is seen in the spectra of six-carbon cyclic hydrocarbons: cyclohexane, cyclohexene, 1,2-cyclohexadiene, and 1,4-cyclohexadiene, shown in Fig. 1. In cyclohexane there is only one kind of carbon, but we see a rich vibrational structure. For the other molecules there are two or three chemically inequivalent carbons and their effects are apparent in the spectra. These results are quite new and have not yet been analyzed. Nevertheless the richness of chemical information is apparent.



**Figure 1** Carbon 1s photoelectron spectra of six-carbon cyclic hydrocarbons

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