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Intensity oscillations in the carbon 1*s* ionization cross sections of 2-butyne

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Carbon 1*s* photoelectron spectra for 2-butyne ($CH_3C{\equiv}CCH_3$) measured in the photon energy range from threshold to 150 eV above threshold show oscillations in the intensity ratio C2,3/C1,4. Similar oscillations have been seen in chloroethanes, where the effect has been attributed to EXAFS-type scattering from the substituent chlorine atoms. In 2-butyne, however, there is no high-Z atom to provide a scattering center and, hence, oscillations of the magnitude observed are surprising. The results have been analyzed in terms of two different theoretical models: a density-functional model with B-spline atom-centered functions to represent the continuum electrons and a multiple-scattering model using muffin-tin potentials to represent the scattering centers. Both methods give a reasonable description of the energy dependence of the intensity ratios. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4810870]

INTRODUCTION

In simplest approximation, the cross section for core-electron ionization by a photon depends on a dipole matrix element that involves both the core and the continuum wave functions. The core orbital is independent of the energy of the photoelectron and, because it is essentially atomic, it can be expected to be independent of the chemical environment. This is, however, not the case for the continuum orbital, which depends on the photoelectron energy and may also be strongly influenced by the structure of the molecule in which the atom is embedded. The first-order effect of the energy dependence is that photoelectric cross sections decrease with increasing photoelectron energy. In addition the effect of the molecular environment may lead to energy-dependent modulations of the cross sections, cross-section ratios, and anisotropies, and such modulations have long been known.[1–8] For the most part, however, these effects have been observed close to threshold, where the cross sections may be strongly influenced by shape resonances.

More recently, it has been noted that energy-dependent modulations of inner-shell cross sections can persist even well above threshold. Such effects were predicted theoretically for carbon 1*s* ionization in a number of molecules by Di Tommaso and Decleva[9] and observed experimentally by Söderström *et al.* in chlorine-substituted ethanes.[6] These results showed that there is an oscillatory behavior of the cross sections as the photon energy increases and that these oscillations can be seen several hundred eV above the ionization threshold. In the work of Söderström *et al.*[6] it was found that the oscillations were associated with the chlorinated carbon atom and that the degree of oscillation increased with

the number of chlorine atoms attached to the ionized carbon. These results were interpreted as arising from EXAFS-type scattering of the outgoing photoelectron from the attached chlorine atoms and it was shown that they could be accounted for quantitatively by a multiple-scattering EXAFS calculation using the FEFF codes.[10, 11]

While it may be reasonable to expect pronounced scattering effects in the presence of heavy atoms such as chlorine, it might not be anticipated that such effects would also play a significant role in molecules containing only first-row atoms. Guided by some preliminary observations of non-stoichiometric intensity ratios in 2-butyne ($CH_3C{\equiv}CCH_3$) and, also, by the predictions of Di Tommaso and Decleva,[9] we have investigated the carbon 1*s* photoelectron spectra of 2-butyne over a range of photon energies from threshold to 150 eV above threshold. Over this energy range we see oscillations in the intensity ratio (C2,3/C1,2) that range from 0.8 to 1.15, indicating that nonstoichiometric cross section ratios will be found even when there is no high-Z scattering center.

These new experimental results also allow us to compare the two theoretical approaches that have been used to account for and predict nonstoichiometric behavior. These are the scattering model used by Rehr *et al.*[10, 11] and the density-functional, B-spline model used by Di Tommaso and Decleva.[9] The model used by Di Tommaso and Decleva is essentially the density-functional equivalent of the "static-exchange"[12, 13] approach to continuum orbitals combined with an atom-centered B-spline basis. Rehr's model uses a Green's function formalism with the scattering contribution to the propagator obtained in an expansion up to a given order of the scattering process, with the atomic

scatterers described in terms of muffin-tin potentials. Also included is a careful treatment of vibrational Debye-Waller damping.

EXPERIMENTAL PROCEDURES AND DATA ANALYSIS

Gas-phase carbon 1s photoelectron spectra for 2-butyne (Sigma-Aldrich, 99%) were measured at photon energies from 295 eV to 450 eV using beamline I411 of the MAX II synchrotron.[14] The sample was outgassed using freeze-thaw cycles, and the sample pressure in the vacuum chamber was maintained at a constant value of about 7×10^{-6} mbar. The electrons were detected and their energies analyzed in a Scienta R4000 analyzer, which was placed at 90° to the beam direction and 54.7° to the polarization direction. At a few energies the sample was mixed with carbon dioxide, which provides a reference line for the energy scale and the instrumental resolution.[15, 16] A typical spectrum, measured at a photon energy of 340 eV, is shown in Fig. 1. The fitting of photoelectron spectra for 2-butyne and related compounds has been discussed in detail by Holme *et al.*[17] and we follow the procedure that they have used. From electronic-structure theory a vibrational profile is calculated for each of the chemically unique carbon atoms in the molecule. These are then convoluted with functions to account for the instrumental broadening (assumed to be Gaussian) and for the combined effects of lifetime broadening and post-collision interaction.[18] The resulting shapes, which are shown in Fig. 1, are then fit to the experimental data using a least-squares procedure.[19] For the two triply bonded carbon atoms in 2-butyne, C2 and C3, there are two core orbitals separated by approximately 100 meV resulting from the bonding and antibonding combinations of the two atomic 1s orbitals. This effect is taken into account approximately by using two identical profiles that are constrained to be 100 meV apart. Two sets of fits were made with different assumptions about the instrumental resolution. In one the Gaussian width was one of the fitting parameters. In this case, the instrumental width was found to vary between 110 meV and 165 meV, depending on the photon energy. In order to test the sensitivity of the results to the resolution a second set of fits was done with the Gaussian width held fixed
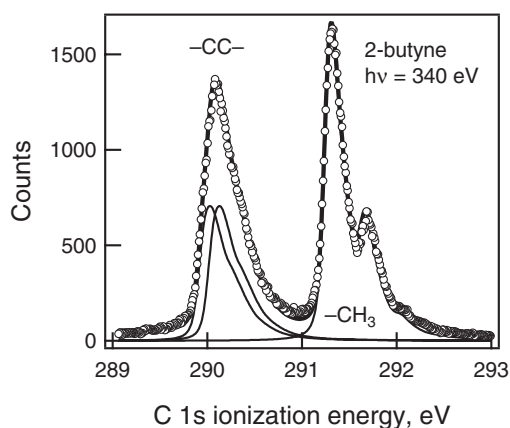
at 100 meV. No significant differences were seen in the intensity ratios between these two fits. The results of the first set of fits are presented here.

The actual photon energy, hν, may differ from the nominal photon energy, hν_0, by as much as 1%, corresponding to 3 or more eV in the region of our measurements. It is, therefore, necessary to calibrate the photon energies. This can be done adding the known adiabatic carbon 1s ionization energies for 2-butyne (C1,4 = 291.291 eV, C2,3 = 290.012 eV[17]) to the measured kinetic energies. For this purpose it is necessary to calibrate the kinetic energy scale of the Scienta analyzer and this calibration has been done using the xenon $N_{4,5}OO$ auger spectrum.[20] With this procedure the photon energies are known to within a few tenths of an eV. The correction, hν − hν_0, ranges from −0.5 eV at a photon energy of 300 eV to −1.20 eV at an energy of 450 eV.

The intensities for photoemission from the two different carbon atoms are obtained from the areas under the peaks. The intensity ratios, C2,3/C1,2, as a function of photon energy and the average photoelectron momentum[21] are shown in Fig. 2. The solid points show the ratios as measured, with different symbols indicating data taken in different years. The statistical uncertainties for the data are less than 1%, which is approximately the size of the symbols in Fig. 2. In addition, since the two peaks in the spectrum are separated by about
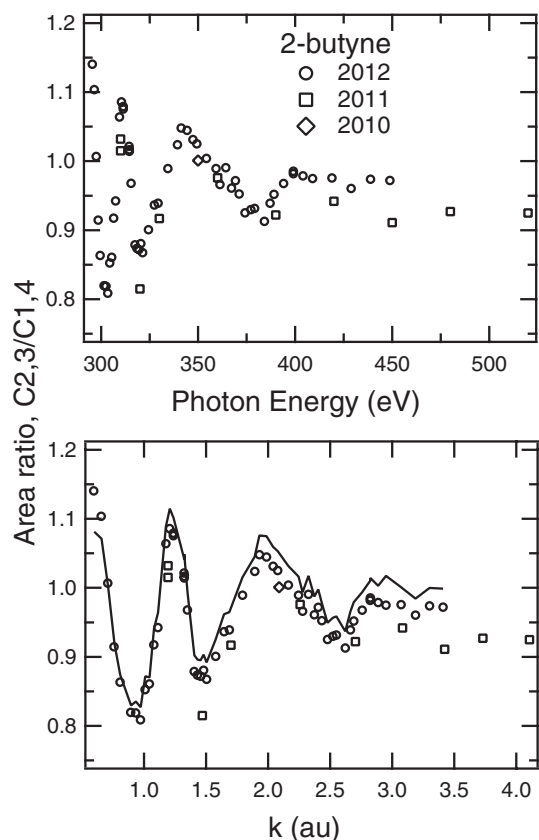
FIG. 2. Intensity ratios (C2,3/C1,4) for the carbon 1s photoelectron spectra of 2-butyne. Different symbols identify data from the indicated years. (Upper) Plotted against the photon energy. (Lower) Plotted against the average photoelectron momentum. The line in the lower graph shows an approximate correction to the 2012 data for the energy-dependence of the transmission of the analyzer.

FIG. 1. Carbon 1s photoelectron spectrum of 2-butyne taken at a photon energy of 340 eV. Open circles show the data. Solid lines show the overall fits and the contributions from individual components.

1.3 eV, it is also necessary to take into account any kinetic-energy dependence of the transmission of the analyzer. At electron kinetic energies above about 10 eV, the transmission function is expected to be smoothly and slowly varying and, therefore, to have only a small effect on the relative intensities. From such data as we have on the transmission function, we estimate that the transmission corrections might be of the order of 3% for kinetic energies above about 10 eV (photon energies >301 eV and $k > 1$ a.u.). The general agreement between the data taken in different years indicates that the transmission corrections are approximately the same from year to year. At energies below about 10 eV, however, the transmission function may depend critically on the voltages applied to the lens elements and the deflector plates of the analyzer. It is possible that the transmission may either increase or decrease as the kinetic energy decreases towards zero.[22–24]

As noted by Jauhiainen *et al.*[22] a comparison of measured and known xenon $N_{4,5}OO$ auger intensities can be used to determine the transmission function over the range of kinetic energies from 8 to 36 eV. Using our data from the 2011 experiments we find that the transmission function is slowly varying over this range and leads to an upward correction of about 3% in the ratios shown in Fig. 2 in this range. Below 8 eV the transmission function is quite uncertain. Unpublished measurements by Canton *et al.*[24] indicate that under some circumstances the transmission goes to zero at zero kinetic energy (although this is not the expected behavior). If we connect our xenon data from 2011 smoothly with zero transmission at zero kinetic energy, then we obtain the solid line shown in the lower panel of Fig. 2. However, it must be emphasized that below 8 eV this correction is quite uncertain. If we use the transmission functions measured by Canton *et al.*, then the ratio at the lowest energies could be as low as 0.75 compared with the uncorrected value of 1.14.

It is apparent from Fig. 2 that there are energy dependent oscillations of the cross section ratio. These are similar to those reported by Söderström *et al.*[6] for chlorinated ethanes, and, specifically, comparable in magnitude to those for 1,1-dichloroethane (CH_3CHCl_2). In the chloroethanes these oscillations have been interpreted as arising from EXAFS-like scattering of the outgoing electrons from the chlorine substituents. This view is supported by the observation that the magnitude of the oscillations increases with the number of chlorine substituents and by theoretical calculations that take this scattering into account. In 2-butyne what appears to be a similar phenomenon must arise from scattering of the photoelectrons by the carbon atoms, primarily those adjacent to the ionized carbon. Since the two central carbon atoms each have two nearest neighbors and the terminal carbon atoms have only one, we expect that this scattering effect will be larger for the central atoms than it is for the terminal ones. More detailed theoretical analysis of these results is presented in section "Theoretical analysis."

THEORETICAL ANALYSIS

Two different theoretical models have been investigated to describe the experimental results. One is based on the method described by Di Tommaso and Decleva,[9] which, as noted above, uses density-functional calculations and atom-centered B-spline wave functions to describe the photoelectrons. The other, developed by Rehr *et al.*[10, 11] uses a Green's function formalism with the atomic scatterers described in terms of muffin-tin potentials.

Density functional model

For the density-functional calculations the multicentric B-spline code has been employed with asymptotic angular expansion up to $L = 24$, which ensures complete convergence of the calculated cross sections. Full details of the method have been previously documented.[25, 26] Two sets of calculations have been made. One is based on time-independent density-functional theory (DFT) and the other on time-dependent density-functional theory (TDDFT).

In Fig. 3 we compare the experimental intensity ratios with the predictions of the two density-functional theoretical models. In this figure we have plotted the intensity ratio versus k, the average momentum of the photoelectron. With some qualifications, there is agreement between theory and experiment. Both show a sharp peak in the intensity ratio for k slightly greater than 1 a.u., but the theoretical results predict a much higher ratio (1.8–2.0) than is observed (about 1.1). An observed dip in the intensity ratio at $k \approx 1.5$ a.u. is reproduced accurately by the theory. A second peak at $k \approx 2$ a.u. is reproduced by the theory, which predicts the position, height, and structure of this peak reasonably well. Beyond $k \approx 2.5$ a.u. the theory shows another peak approximately where one is observed in the data. Overall, the theory predicts the peaks at slightly lower values of k than they are observed in the experimental data, and this trend increases with increasing k. There is little difference between the DFT and TDDFT predictions. If the energy scale for the theoretical calculations is shifted to higher energies by about 3 eV (with a corresponding shift in the values of the momentum) the agreement between theory and experiment is improved. The need for such a shift arises because the exchange-correlation potential employed in the
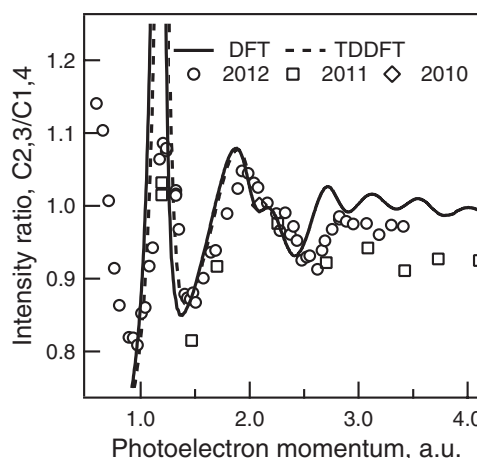

FIG. 3. Comparison between density-functional calculations and experimental values for the intensity ratios (C2,3/C1,4) for the carbon $1s$ photoelectron spectra of 2-butyne. The solid line represents the results of the DFT method and the dashed line represents the results from the TDDFT method.

calculation is slightly too attractive, and shifts the calculated profiles towards threshold.

A more detailed look at the theoretical calculations shows that the strong peak at $k \approx 1$ a.u. arises from ionization of the $2a_1'$ molecular orbital, which is equivalent to a σ_g orbital made from the *gerade* combination of the two $1s$ orbitals of the triply bonded central carbon atoms. This is similar to the behavior seen in ethyne, where the $1\sigma_g$ ionization shows a broad peak in the cross section at a photon energy of about 310 eV ($k = 1.2$ a.u.).[27] By contrast ionization of the $2a_2''$ orbital in 2-butyne shows a monotonically decreasing cross section in this energy region, which is similar to the behavior seen for ionization of the $1\sigma_u$ orbital in ethyne. A strong shape resonance at $k \approx 1$ a.u. is predicted to be a common feature for substituted ethyne molecules such as FCCH, FCCCH$_3$, and FCCCN.[9] The origin of this feature is the presence of a continuum σ_u^* resonance, associated with the ionization of the σ C2C3 antibonding orbital, similar to that seen in the core ionization of N$_2$. Such a feature also appears in the $1a_1'$ ionization, but with much reduced intensity, because of the smaller dipole transition moment from the adjacent methyl C1s orbital.

Multiple-scattering model

The real-space multiple scattering code FEFF9[10,11] was used to calculate the cross sections of each carbon in the molecule. The calculations included self-consistent potentials and employed the full multiple scattering method. Core-hole effects were included using the final state rule, and self-energy effects were neglected. The effects of vibration were accounted for through *ab initio* calculations of the Debye-Waller factors.[28] As FEFF9 does not accurately account for chemical shifts, the ORCA[29] electronic structure code was used with the B3LYP functional to calibrate the shift in the FEFF results to that of the $1s$ orbital energies of the inequivalent carbon atoms. Although this shift is smaller than that found in the experimental results, the results are relatively insensitive except very near the edge. In addition an overall shift (equivalent for both edges) was used to match the average experimental ionization energy.

In Fig. 4 we compare the experimental intensity ratios with the predictions of the FEFF calculations. The agreement between the experimental results and the predictions is similar to that seen for the density functional calculations. The predicted peaks and valleys are approximately where they are found in the experiments. As is the case for the density-functional calculations the ratio for the peak at $k \approx 1$ a.u. is greatly exaggerated in the theoretical results – predicted compared with 1.1 observed. Whereas the density functional calculations predict the peaks to occur at slightly lower k values than observed, the FEFF calculations predict higher k values than observed. In general, the FEFF calculations and the density-functional calculations are in agreement with each other (except for small differences in the energies at which various features are found) and both appear to be in reasonable agreement with the experimental results in the high-energy range.

Two sets of theoretical curves are shown in Fig. 4. The solid line shows results that have not been corrected for the
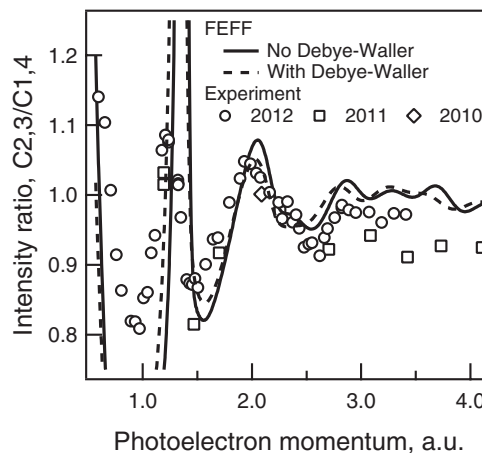

FIG. 4. Comparison between FEFF predictions (lines) and experimental values (points) for the intensity ratios (C2,3/C1,4) for the carbon 1s photoelectron spectra of 2-butyne. The solid line shows results without Debye-Waller corrections and the dashed line shows results that include these corrections.

Debye-Waller effect and the dashed curve shows corrected results. The Debye-Waller correction takes into account the zero-point vibrational motion. As can be seen, its effect is to spread and lower very sharp structures and to damp out the oscillations at high energies. This is particularly noticeable for the peak at $k \approx 1$ a.u., where the height is reduced from 2.8 without correction to 2.3 with correction.

Inelastic corrections

Neither of the theoretical calculations described above contains corrections for inelastic events, which redistribute intensity among different channels, i.e., shake-up and shake-off, associated with multielectron excitations and interchannel coupling. In particular a strong reduction of the spectroscopic factor from the Koopmans value of 1 is associated with core holes, because of the large relaxation involved. If these processes have a differential effect on the different carbon atoms, this will affect the measured ratios. The general agreement between the theoretical prediction and the experimental observations suggests that such differential effects are small. Support for this conclusion comes from a calculation of the contribution of differential relaxation to the difference in carbon 1s ionization energies between the terminal and central carbons (1.28 eV). The extended Koopmans theorem[30] gives an initial-state contribution to this shift of 0.85 eV. This leaves only 0.43 eV due to differential relaxation. The sign of the relative relaxation energy implies slightly greater relaxation for central carbons than for the terminal carbons. This result is consistent with the results seen in Fig. 2, where we see that the asymptotic value of the intensity ratio at high photon energies appears to be close to but slightly less than one.

CONCLUSIONS

The experimental results show that the intensities of the peaks in the photoelectron spectrum of 2-butyne do not necessarily reflect the exact stoichiometry of the molecule, but may differ from this expectation by as much as 20%.

Moreover, the intensity ratio oscillates with the photon energy (or momentum of the photoelectron). This behavior is similar to that seen for chloroethanes,[6] where the chlorine substituents provide strong scattering centers. The current results show that such oscillations and nonstoichiometric intensity ratios can be expected also in cases where there is no strong scattering center. These results have important consequences for the use of photoelectron spectroscopy as an analytical tool.

Comparison of the experimental results with predictions of two different theoretical approaches shows that both methods (which are in general agreement with each other) account well for the overall structure seen in the energy-dependence of the cross-section ratios. In detail, the theoretical models overestimate the magnitude of these effects near threshold. This overestimate is particularly noticeable for the peak at $k \approx 1$ a.u. As noted, this peak arises from the presence of a shape resonance near threshold and it is commonly observed that this level of calculation predicts the profiles of shape resonances to be sharper and more intense than is experimentally observed.

ACKNOWLEDGMENTS

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