

Inner-shell electron spectroscopy and chemical properties of atoms and small molecules

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Executive Summary

The program has been concerned with measuring the gas-phase carbon 1s photoelectron spectra of a number of molecules of potential chemical interest. The primary goals have been to determine carbon 1s ionization energies with a view of relating these to other chemical properties such as electronegativity, acidity, basicity, and reactivity, in order to provide a better understanding of these fundamental properties. With these goals in mind, the project has been concerned with the role of electronegativity in the determining the ionization energies of halogenated methanes, and this work has provided a better understanding of the chemical factors that influence these ionization energies. Similarly, the role of electron-donating (methyl) and electron-withdrawing (fluoro) substituents on the carbon 1s ionization energies of substituted benzenes has been studied. These results have been related to measurements of the reactivities of the same molecule as well as to their affinities for protons (basicity). These comparisons have provided new and clearer insights into the factors that influence these significant chemical properties.

An underlying (and necessary) goal has been to develop the theoretical tools that make it possible to obtain meaningful results from complex and overlapping spectra. Comparison of the experimental and predicted spectra shows that this project has been successful, and that suitable theoretical tools are now available to assist in this analysis.

Opportunities for investigation in unplanned areas have arisen, and the program has been modified to take advantage of these. One has been the realization that, under certain circumstances, inner-shell ionization energies may depend on the molecular conformation. Several examples of this phenomenon have been investigated and it has been shown that this technique provides a tool for the measurement of the energy differences between different conformers of the same substance. The other has been the demonstration that photoelectron recoil can lead to the excitation of vibrational modes that are forbidden in the normal view of photoemission and to rotational heating of the molecule that increases with the energy of the exciting radiation. These results have provided an understanding of previously reported discordant data on ionization energies and have provided a clearer picture of the fundamental processes that give rise to rotational heating.

Goals, accomplishments, and activities

The broad scope of this project has been the study of high-resolution gas-phase carbon 1s photoelectron spectroscopy of a wide range of molecules, with the goal of relating the measured core-ionization energies to other chemical properties. Specific areas that were targeted for investigation were (1) substituent effects, (2) proton affinities and core-ionization energies, and (3) Coulombic effects in photoelectron spectra. Progress was made in all of these areas, as discussed below. In addition, we expanded our research to take advantage of unexpected opportunities in the

areas of conformational effects and recoil effects in photoelectron spectra. Results in these areas are also discussed below.

Substituent effects in substituted benzenes. Two papers have been published and one submitted concerning substituent effects in substituted benzenes. The first of these has dealt with fluorine as a substituent,¹ the second with the methyl group as a substituent,² and the third on the combined effects of both fluorine and the methyl group.³ In these papers we have shown that the effects of multiple substituents on not only carbon 1s ionization energies, but also reactivities and enthalpies of protonation, can be accounted for primarily by a linear additivity model. However, it is also found that there are small but significant nonlinear contributions that must be included in order to have a full description of the substituent effects.

Correlations between core-ionization energies, enthalpies of protonation, and reactivities. In the papers discussed above,¹⁻³ as well as in an additional paper on carbon 1s ionization energies in conjugated aliphatic systems,⁴ we have considered the relationships between carbon 1s ionization energies and other chemical properties, such as enthalpies of protonation and activation energies for electrophilic reactions. All of these processes involve the addition of a positive charge at a localized point in a molecule and it is expected that the energy changes that accompany one of these will be linearly related to the energy changes for another. For 1,3-butadiene and 1,3-pentadiene we have shown that, in keeping with this expectation, there are such linear correlations between the carbon 1s ionization energies and the activation energies for addition of HCl at various positions in the molecule and between the carbon 1s ionization energies and the enthalpies of protonation.⁴ The studies of the fluoro- and methyl-substituted benzenes^{1,2,3} show similar linear correlations, but in some cases there are significant deviations of the data from a single correlation line. In particular, for the correlations between carbon 1s ionization energies and enthalpies of protonation there are four separate but nearly parallel lines for compounds that have 0, 1, 2, or 3 fluorine substituents that are either ortho or para to the site of ionization/protonation. These results can be understood in terms of the role of fluorine as a π -electron donor and the role of the protons at the site of protonation as a π -electron acceptor. Other deviations can be related to steric effects that influence one type of process more than another or to interactions between substituents that lead to nonlinear behavior.

Conformational effects in carbon 1s photoelectron spectra. It had been generally expected that core-ionization energies would be independent of the conformation of the molecule. However, with the improvement in the quality of the experimental data resulting from the use of third-generation synchrotrons and high-resolution electron spectrometers, recent experiments have revealed that, in certain cases, core-ionization energies are dependent on the molecular conformation.^{5,6} A typical example is 1-fluoropropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$, which can exist in two conformers, anti and gauche. In the gauche form the distance between the fluorine atom and the C3 carbon is less than it is in the anti form. Because of the Coulombic interaction between the negative charge of the fluorine and the carbon 1s electrons, the ionization energy of these electrons is about 0.2 eV less in the gauche form than it is in the anti form. This difference is readily apparent in the carbon 1s photoelectron spectra. From the relative intensities of the peaks resulting from each conformer we can calculate the difference in Gibbs free energy between the two conformers, and this agrees with what has been found by other methods. 1-fluoropropane is one example of a class of molecules $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$,

where X is an electronegative group, that show this behavior. We have observed this effect not only for 1-fluoropropane ($X = F$),⁵ but also for $X = C \equiv N$,⁵ $C \equiv CH$,⁶ $C \equiv CR$, Cl, Br, and I. A similar effect is seen in propanal, $CH_3CH_2CH=O$.⁵ It thus appears that these conformational effects are more widespread than had been previously expected and the measurements of these spectra can be used as a tool to measure the energy differences between the conformers.

Recoil-induced internal excitation accompanying photoionization. The atom from which a photoelectron is emitted has a momentum that is equal and opposite to that of the photoelectron. For an atom in a molecule, this momentum is transferred to the molecule as a whole. However, since the molecule has a larger mass than any of its constituent atoms, the recoil kinetic energy of the molecule is less than the recoil energy of the atom from which the electron was ejected. The energy difference is taken up by the molecule as internal excitation, either vibrational or rotational. Although this effect was predicted theoretically more than 30 years ago it is only recently that advances in experimental techniques have made it possible to observe it. Our measurements of the carbon 1s spectrum of CF_4 over a photon energy range from 330 eV (just above threshold) to 1500 eV show that this recoil effect leads to an energy-dependent excitation of the asymmetric stretching mode in the residual ion.⁷ The degree of excitation is found to increase linearly with the kinetic energy of the photoelectron at a rate that is in excellent agreement with the predictions of theory.

For ionization of a core electron it is reasonable that the momentum is taken up initially by the single atom from which the electron is emitted as in the case discussed above. For a valence electron, which is delocalized over the molecule, it is less apparent that this should be the case. To investigate this question we have measured the valence photoelectron spectra of N_2 over a range of photon energies from 60 to 800 eV. For the B state of N_2^+ we find that the recoil-induced rotational excitation increases linearly with the photoelectron kinetic energy at a rate that is consistent with the electron having been emitted from a single atom.⁸ Thus, in this case, the electron acts as if it is localized. For the X state, however, preliminary investigation shows little recoil-induced rotational excitation. This result, which may reflect effects of delocalization, is a subject for future investigation.

During the course of the investigations of recoil-induced internal excitation, we studied the boron 1s photoelectron spectrum of $^{11}BF_3$. Although, in principle, this appeared to be a promising candidate to show recoil-induced excitation, the effect is obscured in this molecule because (1) the photoelectron spectrum shows extensive vibrational structure resulting from excitation of the symmetric BF stretching mode, and (2) because the recoil-induced excitation is more or less equally distributed over three modes – in-plane asymmetric stretching and bending and out-of-plane bending. In spite of these problems we were able to obtain useful data on the symmetric stretching mode and on the lifetime of the boron 1s hole state in BF_3 .⁹

International collaboration

This work has involved an extensive and long-standing collaboration with scientists from the University of Bergen (Norway), the University of Turku (Finland), the University of Uppsala (Sweden), and Tohoku and Sophia Universities (Japan). This has involved both senior personnel as well as a number of graduate students. During the period of the grant, two students from the

University of Bergen, Maria Gundersen and Alf Holme, have spent time at Oregon State University to take advantage of opportunities for enhancing this collaboration. The Master's thesis of Maria Gundersen and the PhD thesis of Velaug Myrseth Oltedal (also of the University of Bergen) have been concerned with work that was carried out with support from this grant.

Doctoral degrees

Velaug Myrseth Oltedal, "Chemical Insights from Carbon 1s Photoelectron Spectroscopy and Theoretical Modeling", University of Bergen, 2007.

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Publications

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