Chemical shifts of carbon 1s ionization energies

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ABSTRACT

Third-generation synchrotrons and high-resolution electron spectrometers coupled with modern theoretical techniques for molecular structure calculations have opened opportunities for measuring carbon 1s ionization energies in a large variety of complex molecules. Recent studies have provided new insights into the chemistry of substituent effects and on the effect of molecular conformation on inner-shell ionization energies.

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1. Introduction

Just over 40 years ago the group at Uppsala, led by Kai Siegbahn, showed that the ionization energies of inner-shell electrons depend on the chemical composition of the molecule under investigation [1,2]. Moreover, they showed that these chemical shifts are very closely related to such basic chemical concepts as ionicity and electronegativity. Later studies showed that the shifts were also influenced by the polarizibility of the molecule. Because these concepts – ionicity, electronegativity, and polarizibility – are fundamental to the understanding of chemical properties there was considerable activity by chemists in investigating these shifts. The decade of the 1970s yielded a wealth of both experimental and theoretical investigations of chemical shifts in a variety of compounds. Many of the results of these investigations have been summarized in a compilation by Jolly et al. [3].

Missing from this outpouring of results were investigations of carbon 1s ionization-energy shifts in all but the simplest organic molecules. At this time the experimental resolution was not sufficient to determine these energies in molecules containing several chemically inequivalent carbon atoms. Early work on chemical shifts of carbon 1s ionization energies was therefore largely limited to situations where there was an electronegative substituent attached to a carbon atom. As a result, only limited information could be obtained on many systems of considerable chemical significance, for instance substituted benzenes.

During the last 15 years there has been a profound change in this situation. Third-generation synchrotrons have provided photons at energies above the carbon edge with very high resolution. Combining this capability with that of high-resolution spectrometers, such as those pioneered at Uppsala under the guidance of Kai Siegbahn, has made it possible to measure carbon 1s ionization energies with instrumental linewidths as narrow as half of the carbon 1s natural linewidth (70–100 meV in free molecules). The results of such measurements together with the results of modern electronic and molecular structure calculations have made it possible to obtain carbon 1s ionization energies for all of the inequivalent carbon atoms even in molecules with as many as eight inequivalent carbon atoms and with chemical shifts of only a few 10's of meV. These results have provided insights into substituent effects in a number of chemically significant molecules [4–19].

Most of these experiments have focused on the effects of chemical composition on the ionization energies. It has, however, been recognized that the molecular conformation might also affect inner-shell ionization energies [12,13,20,21], but evidence for effects of conformation on the photoelectron spectra of isolated molecules has been available only in the last few years [22–27].

In the following we review some of the recent results for high-resolution measurements of carbon 1s ionization energies and discuss how these can be used to provide insights into chemical properties of organic molecules. In addition we present some previously unpublished results where these are useful in developing a particular point.

2. Methods

Details of the experimental and theoretical procedures as well as of the analysis techniques can be found in the original papers [7,9,10,14–19]. Here we present only a brief summary.

2.1. Experimental methods

The experimental measurements of carbon 1s photoelectron spectra have been carried out at the Advanced Light Source, using one of the branches of beamline 10, and at the MAX II synchrotron, using beamline I411. Most measurements were made at a photon energy of 330 eV, which is close enough to threshold that the intensity and resolution are good and far enough above threshold that effects of post-collision interaction, though noticeable, are not large. The electrons were detected and their energies analyzed in Scienta SES 200 analyzers. The overall instrumental resolution in these experiments has ranged from 35 to 90 meV. Calibration of the ionization energies was obtained by running the samples of interest mixed with either CO_2 or CF_4 for which the ionization energies are known [28].

2.2. Theoretical methods

Analysis of the experimental spectrum, which often involves a number of overlapping peaks, requires a prediction of the vibrational excitation that accompanies core ionization. For this purpose we need the vibrational frequencies, normal-mode vectors, and geometries of the neutral and ionized molecules [29]. For these we have relied on theoretical calculations using the Gaussian set of programs [30]. For hydrocarbons and fluorohydrocarbons we have used the B3LYP density functional method, a triple-ζ basis set, and, to represent the core hole, an effective core potential (ECP) to provide the required frequencies, normal-mode vectors, and geometries. Comparison of the results of these calculations with those of higher level calculations indicates that this method overestimates the bond shrinkage of CH bonds attached to the ionized carbon by about 0.3 pm, and, therefore, the predicted bond-length changes have been adjusted accordingly. Similar comparisons indicate that this method overestimates the CH vibrational stretching frequencies by about 5% for CH bonds attached to the ionized carbon, and, therefore, these predicted CH stretching frequencies have been scaled accordingly. Franck-Condon factors to describe the vibrational excitation have been calculated using the harmonic-oscillator approximation, except for the CH stretching modes, which are often strongly excited. For these modes we have calculated the Franck-Condon factors using the wave functions of a Morse potential. This procedure gives predictions of the vibrational excitation that are generally in good agreement with the experimental results. Typical examples are shown in subsequent sections. For other molecules, such as those containing chlorine or a carbonyl group, evidence is beginning to accumulate (see below) that more sophisticated techniques such as CCSD(T) are needed.

In addition to providing information on the vibrational excitation accompanying core ionization, these calculations also give theoretical predictions for the ionization-energy shifts. These have been found to be generally in good agreement with those observed experimentally, but there remain some systematic deviations between experiment and theory [14,16–19] that are the subject of ongoing investigations.

2.3. Analysis procedure

The experimental photoelectron spectra are fit using the least-squares method with line profiles representing the predicted vibrational structure for each kind of carbon atom in the molecule [31]. These line profiles are convoluted with Gaussian functions to represent the instrumental resolution and with a function [32] to represent the combined effects of the lifetime of the core hole and the post-collision interaction (PCI) between the photoelectron and the Auger electron that is emitted from the core-ionized molecule. The only adjustable parameters in these fits are the overall intensities and positions for the profiles representing the contributions from each chemically unique atom.

3. Some typical results and the problems they present

Spectra of five simple molecules – methane, ethane, fluoroethane, benzene, and fluorobenzene – provide an overview of the features that are apparent in high-resolution carbon 1s photoelectron spectra. One of these is the line shape, which includes a Gaussian component reflecting the instrumental resolution, a Lorentzian component reflecting the carbon 1s linewidth, and possible distortion of the peak shape arising from PCI. Another feature is the possible presence of chemically inequivalent carbon atoms in the same molecule, which gives rise to two or more peaks that contribute to the observed spectrum. Thirdly, there is vibrational structure associated with each peak, and this provides a useful tool for associating each peak with the appropriate carbon atom and an aid in analyzing the spectra. Finally, for ethane and benzene, which have adjacent equivalent carbon atoms it is necessary to take into account the splitting of the carbon 1s molecular orbitals and the effect of vibronic coupling, which can break the symmetry of the molecule.

3.1. Methane and ethane

Methane and ethane are the simplest hydrocarbons. Understanding their carbon 1s spectra provides the basis for understanding the spectra of more complex molecules, many of which have a hydrocarbon skeleton as the underlying structure.

The carbon 1s photoelectron spectrum of methane was shown by Siegbahn and co-workers to have vibrational structure arising because of the change in the carbon–hydrogen equilibrium bond length upon ionization [33–35]. Since their discovery of this phenomenon, methane has been the subject of numerous investigations, each reflecting advances that had been made in resolution at the time. At photon energies close to threshold the spectrum shows a simple vibrational progression arising from excitation of the symmetric carbon–hydrogen stretching mode. This spectrum is well understood from a theoretical point of view, although a complete understanding has required the inclusion of the effects of Fermi resonance, anharmonicity, and core-valence electron correlation [36–38]. At high photon energies there are also contributions to the spectrum from recoil-induced excitation of nonsymmetric modes [39].

Ethane provides the next level in the complexity of the saturated hydrocarbons. Here there is the possibility of exciting not only the symmetric carbon–hydrogen stretching mode, but also the carbon–carbon stretching mode as well as HCH bending modes. The carbon 1s photoelectron spectrum of ethane [40] is illustrated in Fig. 1A, where the open circles show the experimental data and the solid line shows the theoretically calculated profile. The significant point to note is that the theoretical profile, calculated as outlined above and with no free parameters other than overall position and height, fits the observed shape quite well.

In the conventional molecular orbital picture, the two carbon 1s atomic orbitals in ethane combine to give bonding and antibonding molecular orbitals that are split by about 18 meV. Because of the near degeneracy of these orbitals vibronic coupling leads to localization of the core hole onto one of the carbon atoms