Conformational Effects in Inner-Shell Photoelectron Spectroscopy of Ethanol

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(Received 5 February 2005; published 2 September 2005)

The carbon 1*s* photoelectron spectrum of ethanol shows two peaks, one for the methyl carbon and one for the functionalized carbon. While the peak shape for the functionalized carbon is readily understood, the shape for the methyl carbon requires that there be comparable contributions from both the *anti* and *gauche* conformers of ethanol and that the torsional motion in the HOCC dihedral angle be strongly excited upon core ionization. An accurate description of the peak shape requires a high level of electronic-structure theory together with consideration of anharmonicity and coupling of the torsional motion with other vibrational modes.

DOI: 10.1103/PhysRevLett.95.103002 PACS numbers: 33.20.Tp, 33.60.Fy, 33.70.Jg

Chemical effects on inner-shell ionization energies and, hence, on inner-shell photoelectron spectra have long been known and have been a source of insight into a variety of chemical phenomena. In addition, each inequivalent atom in a molecule has a unique vibrational structure associated with it in the photoelectron spectrum. This structure is a source of information on the potential energy surface of the core-ionized molecule and on the dynamics of the ionization process.

Some molecules may exist in a number of conformations, corresponding to different degrees of internal rotation of one molecular fragment relative to another. Determination of the conformations of small biological molecules in the gas phase has recently become a hot research topic. Various experimental techniques are used to this end, including that of advanced UV and IR/UV double resonance spectroscopies [1–3]. Up to now, there has been little reason to expect that different conformers would have different core-level photoelectron spectra, and where this possibility has been investigated, no such effects were observed [4]. By contrast, we present here experimental and theoretical results that show just such effects in the carbon 1*s* photoelectron spectrum of ethanol. Moreover, based on our analysis of the physical origin of these effects, we expect that conformational effects may be fairly common in core-level spectra of small molecules that exhibit conformational equilibria and possibly of use in resolving conformational issues.

We consider the carbon 1*s* photoelectron spectrum of ethanol shown in Fig. 1. The corresponding spectrum of chloroethane has been added for comparison. Since the electronegativity of chlorine is similar to that of the hydroxyl group, one may anticipate that differences between the two spectra are associated with the additional three vibrational degrees of freedom contributed by the OH group as compared to chlorine.

At high ionization energy, i.e., to the right in Fig. 1, the two spectra display very similarly structured peaks corresponding to the functionalized carbons, each showing a small peak due to CH stretching and a shoulder due to CC stretching as well as bending modes. The parts of the spectra that correspond to the methyl groups (on the left) are, by contrast, rather different. For chloroethane, there is evidence for CH stretching, giving rise to a second peak with lower intensity. By contrast, the methyl peak for ethanol is broad and rather featureless.

The difference between the ethanol and chloroethane spectra can be understood if we recognize that ethanol exists in two conformers, *anti* and *gauche*, illustrated in Fig. 2, while chloroethane exists in only one (staggered) conformation. In the *anti* form of ethanol, the hydrogen of

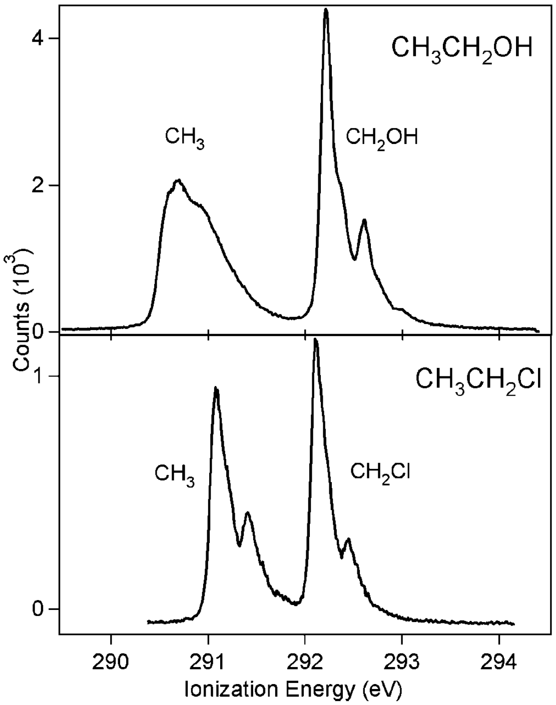

FIG. 1. Experimental carbon 1*s* photoelectron spectra of ethanol (top panel) and chloroethane (bottom panel).

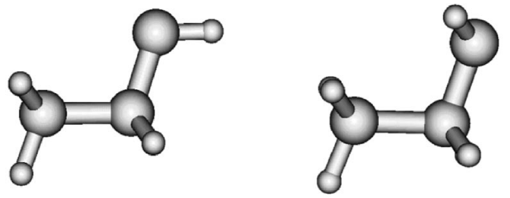

FIG. 2. Geometric structures of *anti* (left) and *gauche* ethanol (right) conformations.

the hydroxyl group is relatively far from the methyl group and is unaffected by ionization of the methyl group. In the *gauche* conformer, on the other hand, the positively charged hydroxyl proton is relatively close to the methyl group. When the 1s electron of the methyl carbon is ionized, there will be strong repulsion between the positive charges of the hydroxyl proton and the methyl group, resulting in internal rotation from the *gauche* to the *anti* configuration and strong excitation of the HOCC torsional mode. Thus, ionization of the methyl group in ethanol leads to two qualitatively different components in the spectrum, one from the *anti* form and one from the *gauche* form. Moreover, ionization of the *gauche* form leads to a broad spectrum, since there is considerable excitation of the torsional mode.

The foregoing explanation, while plausible, needs support. Here we present a theoretical model of this spectrum and show that the ideas expressed above are essentially correct and that we have observed the first example of a conformational effect on an inner-shell photoelectron spectrum. We will see, however, that the calculations are far from simple and that it is necessary to use a high level of electronic-structure theory, to consider anharmonicity (especially in the torsional mode), and to take account of coupling between the HOCC torsional mode to other vibrational modes, such as hindered rotation of the methyl moiety and CCO bending.

The carbon 1s photoelectron spectra of ethanol was measured on beam line 10.0.1 of the Advanced Light Source in Berkeley, USA. The ethanol measurements were repeated along with measurements of the carbon 1s spectrum of chloroethane at beam line I411 of the MAX II synchrotron facility in Lund, Sweden [5]. In both cases the electron spectra were measured using a Scienta SES-200 electron-energy analyzer. The photon energy was 330 eV. The monochromator and electron-energy analyzer slits and the pass energy of the analyzer were chosen to give an overall experimental broadening of about 75 meV. Calibration of the ionization energy scales is based on simultaneous measurements of the carbon dioxide carbon 1s spectrum [6].

Our usual way of analyzing a gas-phase photoelectron spectrum involves calculation of the equilibrium geometries and normal modes for the neutral and core-ionized molecules [7,8]. Franck-Condon factors are calculated for each mode using the harmonic-oscillator approximation. The one-dimensional vibrational profiles for each mode are convoluted with each other to provide an overall vibrational excitation spectrum, and the resulting bar spectrum is subsequently convoluted with broadening functions that reflect the natural linewidth, Gaussian resolution, and the interaction between the photoelectron and the Auger electron emitted in the deexcitation of the core-hole state. This interaction is described using Eq. (12) from van der Straten *et al.* [9]. These profiles (one for each different core-ionized carbon) are fit by least-squares techniques [10] to the experimental data with the position and height of each profile as a fitting parameter. In detail, some empirical corrections to the calculated vibrational frequencies and bond-length changes must be included to correct for inadequacies of the theory [8]. Moreover, as in previous studies, small corrections for the anharmonicity of CH stretching modes has been made by describing these modes in terms of Morse potentials.

For ethanol, the harmonic approximation does not provide a satisfactory description of the torsional motion about the OC bond, especially when the methyl group has been core ionized. As a better approximation, we have calculated the one-dimensional potential for this torsional motion for the neutral molecule and for the core-ionized molecule; see Fig. 3. From these potentials, the vibrational wave functions were determined numerically [11] and used to evaluate the appropriate Franck-Condon factors.

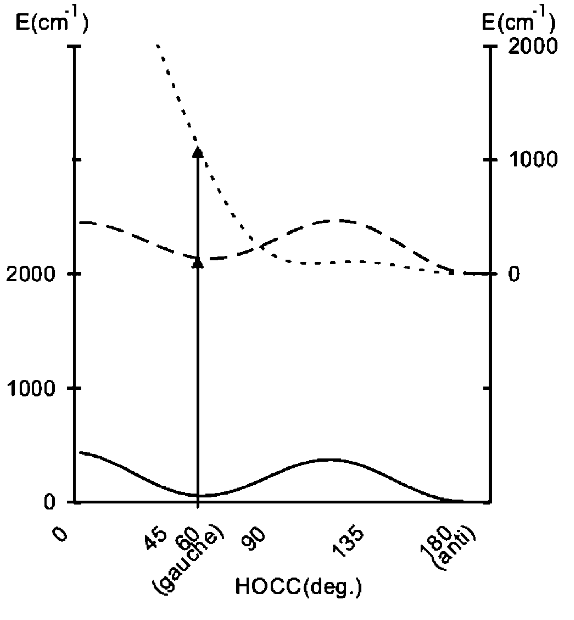

FIG. 3. Potential energy in the HOCC torsional mode, for the ground state of ethanol (solid line, plotted at the *left* value axis) and the C1s-ionized molecules (dotted line, ionized at the CH_3 carbon; dashed line, ionized at the CH_2OH carbon; both plotted at the *right* value axis). The arrows indicate vertical ionization of the *gauche* molecule, at either of the two carbon sites.

In Fig. 4, the experimental and theoretical spectra for ethanol are compared. To obtain the theoretical profile, the calculations were first done using the B3LYP method [12] in conjunction with Dunning triple-ζ basis sets augmented with 6-311G(*d, p*) polarization functions [13,14]. The core hole was described using an effective core potential [15,16]. For each site of ionization, two profiles were calculated, one for the initial molecule in the *anti* configuration and one for the *gauche* configuration.

The four profiles, i.e., one for each conformation and each site of ionization, are fit by least squares to the experimental data with the four positions and the *gauche* and *anti* intensities as fitting parameters. The common ratio of areas of the *gauche* to *anti* profiles is used for both sites of ionization. A constant background is also a fitting parameter.

For ionization of the functionalized carbon [right-hand peak in Fig. 4(a)], the computed spectra for the two conformers are nearly identical, and together they reproduce the observed peak shape reasonably well. By contrast, for ionization of the methyl carbon the profiles for the different conformers are quite different. For ionization of the *anti* conformer, the profile is structured and shows clearly the contribution from the CH stretching mode. For ionization of the *gauche* conformer, the theoretical profile is broad and featureless, consistent with a high degree of vibrational excitation upon ionization. While the theoretical approach outlined thus far accounts for the major features of the spectrum, it does not agree in detail with the experimental spectrum: The shoulder that appears at low binding energy in the methyl peak of the spectrum is not present in our theoretical model, and, moreover, the model predicts a well-defined second maximum rather than a pronounced shoulder to the right of the maximum of the methyl carbon peak. Apparently, the theoretical model may be improved in several respects. Indeed, in order to be practical, the theoretical calculations involve compromises in both the electron structure part (choice of basis sets, electron correlation method, and representation of the core hole) and, more severely, the treatment of anharmonicity in the vibrational problem.

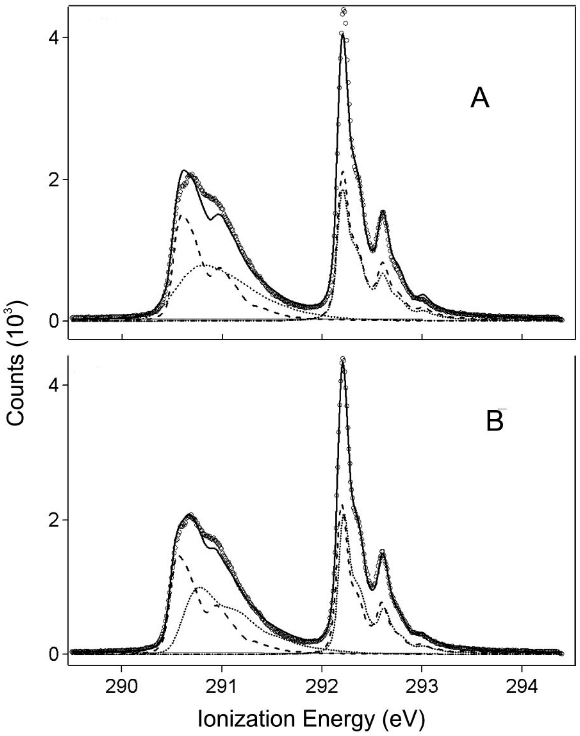

FIG. 4. Experimental (circles) and theoretical (solid lines) carbon 1*s* photoelectron spectrum of ethanol. Parts (a) and (b) correspond to the basic and extended theoretical models, respectively. The individual contributions from the *anti* (dashed lines) and *gauche* (dotted lines) conformations of ethanol are also shown.

In order to verify our analysis of the spectrum at hand, we decided to extend the theoretical model to address the compromises that were made in the first model. The details of this treatment will appear in a subsequent paper [17], and only the results will be summarized here. The principal effect of improving the electronic-structure description is to reduce the excitation of CC and CO stretching modes, leading to excellent agreement between the observed and calculated spectra for the functionalized carbon.

A detailed analysis indicates that the broad profile resulting when the *gauche* conformer is ionized arises not only from excitation of the HOCC torsional mode but also from anharmonic coupling of this mode to the other modes. Inclusion of anharmonic mode coupling leads to very good agreement between theory and experiment also in the case of the methyl carbon, and represents a significant improvement over the simpler model. In Fig. 4(b) the experimental spectrum is shown together with model spectra pertaining to both *gauche* and *anti* conformers. As can be seen, the low-energy shoulder of the spectrum is now accounted for, while the flattening on the high-energy side of the methyl peak remains somewhat exaggerated.

Up to now, we have disregarded the presence of thermal excitation in the two conformations. In fact, the lowest excited state ($\nu = 1$) of the HOCC torsional mode is thermally populated in both the *anti* and *gauche* conformations. Still, the thermal excitation hardly affects the line shape of the photoelectron spectrum. In the *anti* case, this may be understood from the fact that the potential curves in Fig. 3 are almost parallel near the *anti* geometry. For the *gauche* conformation, the line shape is governed by projection of a well-localized wave function on a set of final states which are delocalized in space and fairly densely spaced in energy. Although the $\nu = 1$ initial-state wave function is less localized than the *gauche* ($\nu = 0$) function, the modest changes in the Franck-Condon factors are effectively camouflaged by the broad nature of the spectrum. Moreover, since the amount of thermal excitation is almost the same for the two conformations, the *gauche*-*anti*–intensity ratio may be interpreted within a two-state Boltzmann model, i.e., without taking explicit notice of the thermal excitation. Our estimate of the *gauche-anti*–energy difference becomes 18 meV, which is somewhat high compared to values obtained in a direct calculation using 4th order Möller-Plesset theory (6 meV) [18] or from microwave spectroscopy (5 meV) [19].

An alternative approach to this energy difference appears from recognizing that ionization of the methyl carbon in each of two conformations leads to a common adiabatic final state, in the *anti* conformation. This method is very sensitive to shortcomings in the theoretical description of highly excited vibrational states, and the resulting *gauche-anti* splitting, in the order of 100 meV, is clearly too large.

The line shape of the methyl C1*s* photoionization line in ethanol is significantly influenced by the presence of two conformations. The effects on the ionization energies are small and difficult to resolve because of strongly overlapping peaks for the two conformations. Rather, the differences lie in the vibrational profiles, i.e., the vibrational excitations accompanying the ionization process. This takes on some resemblance to IR/UV double resonance spectroscopy, in that the vibrational spectrum provides a fingerprint of each electronically excited conformation. Another common feature is that quantum chemical modeling of the vibrational properties of the conformations is required to extract the conformational information from the spectra. In our case, deconvolution of the spectrum by means of theoretical line shapes pertaining to each of the conformations, opens for semiquantitative estimates of the relative populations.

Equipped with insight from the present study, we have found further evidence for conformational effects in carbon 1*s* photoelectron spectra of several other small molecules, including alcohols, amines, and alkynes. Based on these examples, significant conformational effects in a core-level photoelectron spectrum may be expected if two or more conformations are present in comparable amounts in the ground state, and if core ionization of at least one atom leads to large differences in geometric relaxation between the conformations.

We are pleased to thank John Bozek and Maxim Tchaplyguine for their assistance at the ALS and MAXLAB, respectively. Support was received from the Research Council of Norway, the European Community—Access to Research Infrastructure Action of the Improving Human Potential Programme, NORDFORSK—Nordic Research Board, and the Norwegian High Performance Computing Consortium NOTUR. M. A. thanks The Norwegian State Educational Loan Fund for financial support.

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