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Laboratory frame electron angular distributions – a sensitive probe of chemical environment through intramolecular electron scattering

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Abstract

Carbon 1s photoelectron asymmetry parameters β for the chlorinated and the methyl carbon atom of $\text{CH}_3\text{CH}_2\text{Cl}$, CH_3CHCl_2 , and CH_3CCl_3 have been measured using synchrotron radiation in the 340–600 eV energy range. We provide experimental evidence that the intramolecular scattering strongly affects β values, even far from the ionization threshold. The results are in agreement with B-spline DFT calculations, making it possible to single out the behavior of the various continuum partial waves. We conclude that the intramolecular scattering makes electron angular distributions a sensitive probe of the chemical environment, even in isolated gas phase molecules.

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A recent study by Söderström *et al.* [1] revealed the existence of oscillations in the C 1s photoionization cross section ratios of two inequivalent C atoms in gas phase chloroethane ($\text{CH}_3\text{CH}_2\text{Cl}$), 1,1-dichloroethane (CH_3CHCl_2), and 1,1,1-trichloroethane (CH_3CCl_3) as a function of photon energy. The measured ratios were far from the stoichiometric expectations and the oscillatory behavior was shown to persist up to several hundred eV above the photoionization thresholds. The observed oscillations of the intensity ratios were enhanced when more H atoms were replaced by Cl atoms, and were interpreted as EXAFS-type of modulations mainly due to the scattering from the Cl atoms. A computational study of the nonstoichiometric behavior of C 1s cross sections in different hydrocarbons has been carried out by Di Tommaso and Decleva [2]. They predicted a strong oscillatory behavior in the intensity ratios: i) sharp structures close to the ionization thresholds due to shape resonances, ii) smoother non-vanishing oscillations at higher energies due to the scattering from neighboring atoms. Even earlier, Natalense *et al.* [3] have compared the angular dependence of the C 1s photoionization cross sections in CH_4 , CF_4 , and CCl_4 , close to threshold. They pointed out that the complete replacement of H by F and Cl remarkably modifies the C 1s cross sections and asymmetry parameters. While shape resonances [4] were known to affect the angular distributions of photoelectrons [5], more recently vibrationally specific cross sections and photoelectron angular distributions have been shown to strongly deviate from the Franck-Condon behavior close to the photoionization thresholds (see e.g. [6, 7] and references therein). In this Letter the angularly resolved C 1s photoelectron spectra and asymmetry parameters β for two inequivalent carbon atoms in $\text{CH}_3\text{CH}_2\text{Cl}$, CH_3CHCl_2 , and CH_3CCl_3 are discussed. The measurements were performed with photon energies 340, 360, 400, and 600 eV, to avoid the vicinity of shape resonances. We observe a strong x-ray polarization dependence in intensity ratios of the chlorinated ($\text{CH}_x\text{Cl}_{3-x}$, $x=0,1,2$) versus the methyl group (CH_3) C 1s lines, reflected in the β parameters, which exhibit a high sensitivity to the chemical environment of the emitter.

The experiment (see Supplemental Material [8] for details) was carried out at the PLEIADES beamline [9–12] at the SOLEIL national synchrotron radiation facility in Saint-Aubin, France. The Apple II permanent magnet HU80 (80 mm period) undulator was used to provide linearly polarized light with 0° , 90° , and 54.7° between the polarization vector and the electron detection axis. The C 1s photolines were recorded using a wide angle lens VG-Scienta R4000 electron energy analyzer installed on the C-branch of the beamline [10].

FIG. 1. C 1s photoelectron spectra of a) $\text{CH}_3\text{CH}_2\text{Cl}$, b) CH_3CHCl_2 , and c) CH_3CCl_3 measured with 0° (light) and 90° (dark) polarizations and 340 eV photon energy. The spectra are normalized with respect to acquisition duration, photon flux, and gas pressure. All spectra acquired at 90° are multiplied by a factor of 3 for easier visual comparison.

Figure 1 presents the C 1s photoelectron spectra recorded with 340 eV photon energy with 0° and 90° polarizations. The K-shell ionization of the chlorinated C leads to a photoline of higher binding energy as compared to the methyl C 1s photoline. As already reported in Ref. [1] for 54.7° polarization, the intensity ratios of chlorinated and methyl C 1s photolines vary as a function of photon energy due to intramolecular scattering. Now the effect of scattering is clearly evidenced at a given photon energy but between two different polarizations. For example, if we compare the CH_3CCl_3 spectra measured at 340 eV (Fig. 1c), it is seen that the photoline of chlorinated C is obviously enhanced at 90° as compared to the methyl C photoline. The same holds for CH_3CHCl_2 and $\text{CH}_3\text{CH}_2\text{Cl}$, as well as for different photon energies, the enhancement being gradually less pronounced when the degree of Cl substitution decreases.

A simple physical picture describing the effect of scattering on the electron angular distributions is depicted in Fig. 2 for different polarizations and ionization continua. CH_3CCl_3 is

FIG. 2. Simple model illustrating the effect of intramolecular scattering, making photoelectron angular distribution more isotropic in the laboratory frame. For CH_3CCl_3 a C $1s$ photoelectron can be emitted as an a) E or b) A_1 symmetry wave. The grey double arrow shows the orientation of the $\mathbf{e}$ vector and thus the preferential emission direction of the photoelectrons in the dipole approximation. Small curved arrows depict the redirected electrons due to the scattering from the neighboring atoms. Two molecular orientations are considered for each angle between the electron detection axis and $\mathbf{e}$ (0° and 90°).

selected as an example, but the discussion is also applicable to $\text{CH}_3\text{CH}_2\text{Cl}$ and CH_3CHCl_2 . The C $1s$ orbitals in CH_3CCl_3 (C_{3v} symmetry) are $2a_1$ (chlorinated C) and $3a_1$ (methyl C) (the corresponding orbitals are $2a'$ and $3a'$ in $\text{CH}_3\text{CH}_2\text{Cl}$ and CH_3CHCl_2 , both of C_s symmetry). The ionization of an a_1 orbital leads to a continuum wave of A_1 or E symmetry (see detailed discussion in [8]). In the dipole approximation the E continuum will preferentially “select” the molecules with their molecular axis perpendicular to the polarization vector $\mathbf{e}$, and thus parallel to the electron detection axis for the 90° scheme (Fig. 2a). The crude central potential model approximation leads for C $1s$ photoionization to the ideal energy independent $\beta = 2$ parameter [13], the electrons being emitted with a $\cos^2 \theta$ distribution,

θ being the angle between the photoelectron momentum and the $\mathbf{e}$ vector. As $\mathbf{e}$ is perpendicular to the detection axis, no signal should be detected. However, this is not the case experimentally. In addition to the well-known relativistic or non-relativistic (anisotropic) electron-ion or configuration interactions extensively discussed for atoms [13, 14], the origin of the present observation is a molecular effect. The emitted electrons are scattered by the surrounding atoms, which affects their angular distribution and allows some of them to reach the detector. In the present case, since the scattering cross section is smaller for H than for Cl, the relative signal from the chlorinated C is larger than from the methyl C at 90° (see Figs. 1 and 2). Correspondingly, a decrease of the electron signal in the 0° detection scheme will be observed. In the case of the A_1 continuum, the molecules with the molecular axis parallel to the $\mathbf{e}$ will be preferentially “selected” and a discussion analogous to the above leads to similar conclusions (Fig. 2b).

To model the role of the intramolecular scattering on the laboratory-frame electron angular distribution, the photoionization observables (cross sections and asymmetry parameters) have been computed employing a DFT approach (see details in [8]). Figure 3 illustrates the photoionization cross sections of the chlorinated C $1s$ ($2a_1$ and $2a'$) and methyl C $1s$ ($3a_1$ and $3a'$) orbitals for $\text{CH}_3\text{CH}_2\text{Cl}$, CH_3CHCl_2 , and CH_3CCl_3 . All cross sections show similar oscillatory behavior, but the amplitude of the oscillations are the largest for CH_3CCl_3 and the smallest for $\text{CH}_3\text{CH}_2\text{Cl}$. A surprisingly sharp first peak, seen in the $2a_1$ and $2a'$ cross sections, is assigned to a shape resonance, whereas in the $3a_1$ and $3a'$ cross sections a smooth oscillatory behavior is observed already at the lowest photon energies. The second clear peak observed in the $2a_1$ and $2a'$ cross sections is located too high in energy (~ 60 eV above threshold) to be assigned to a shape resonance, and it is interpreted to be the first unambiguous fingerprint of intramolecular scattering. Contrary to the cross section oscillations typical of the coherent emission from equivalent centers [15], the oscillatory structures of the chlorinated and methyl C $1s$ cross sections are not in phase opposition. In the $2a_1$ and $2a'$ channels the oscillations have significantly longer periods and larger amplitudes compared to the $3a_1$ and $3a'$ channels, which exhibit more regular and less damped structures.

The inset in the Fig. 3 shows the partial E and A_1 continua contributions to the $2a_1$ and $3a_1$ photoionization cross sections of CH_3CCl_3 . For $2a_1$, the largest contribution comes from the E channel due to its two-fold degeneracy; the A_1 channel shows a modest contribution to the sharp peak around 350 eV, and then it is mostly flat. Interestingly, it also shows a

FIG. 3. Theoretical C 1s photoionization cross sections corresponding to the ionization of the chlorinated (solid lines) and the methyl carbon (dashed lines) of $\text{CH}_3\text{CH}_2\text{Cl}$ (green), CH_3CHCl_2 (red), and CH_3CCl_3 (blue). The pink and black solid and dotted lines in the inset show the contributions of A_1 and E continuum channels in the case of CH_3CCl_3 (see text for details).

lower energy structure before 350 eV, which is however hidden by background in the total cross section. For $3a_1$, both A_1 and E channels show important oscillations, generally not in phase, and therefore the oscillations in the total cross section come from the superposition of the two different contributions. The lowest energy oscillations are associated with the E channel. Oscillations in the A_1 channel persist even at high energies, whereas in the E channel they are more strongly damped.

Based on the above analysis, we assign the features observed in the A_1 channel mostly to electron diffraction by the neighboring C atom, as it corresponds to photoelectrons mainly ejected along the C-C bond. The E component is mostly sensitive to the surrounding Cl atoms (the H atoms having a minor effect), since the photoelectron escapes mainly in the perpendicular direction (as seen in Fig. 2). This explains the larger amplitude of the oscillations and the longer period in the $2a_1 - E$ channel as compared to $3a_1$ (shorter C-Cl distance). A much smaller effect is seen in the A_1 component of the $2a_1$ cross section.

However, the lowest energy feature could be a signature of the diffraction by the other C atom. In contrast, the electron ejected from the $3a_1$ orbital is diffracted with similar intensity by both the other C and the Cl atoms (note that the Cl-group has also an a_1 component, contributing to the scattering of the a_1 continuum wave), so both A_1 and E components have similar oscillation amplitudes.

The experimental asymmetry parameters β were extracted for both chlorinated and methyl group carbons using data from the 0° and 90° measurements. This method requires a careful normalization of the experimental spectra in order to obtain the intensities I_{0° and I_{90° (areas of the C 1s photolines) independent of photon flux, gas pressure, or data collection time. To obtain β , the following formula was used:

$$\beta = 2[I_{0^\circ}/I_{90^\circ} - 1]/[I_{0^\circ}/I_{90^\circ} + 2] \quad (1)$$

where I_θ is the intensity measured at the indicated angle. An alternate method described by Kivimäki et al. [16] uses the 0° and 90° together with measurements performed at so-called “magic angle”, 54.7° , where the photoionization cross-section is independent of β . With this method there is no need for normalization to account for the experimental conditions. We have also used this method to calculate the values of β , which are in agreement with those obtained by the method described above. However, the uncertainties obtained by the latter method are large if β_{CH} and β_{CCL} are nearly equal (as in our case at high photon energies). Therefore, these results are not shown.

Figure 4 presents the theoretical and the experimental β values for C 1s photoionization in $\text{CH}_3\text{CH}_2\text{Cl}$, CH_3CHCl_2 , and CH_3CCl_3 . In addition, the theoretical β parameter for C 1s photoionization of ethane (C_2H_6 , an average β from the $1a_{1g}$ and $1a_{2u}$ ionization cross sections) has been plotted together with the methyl group β , offering a “Cl-free” reference. The asymmetry parameters for the chlorinated carbon show a clear trend, CH_3CCl_3 showing the largest β -variation in the considered energy range. The changes in the methyl C β values are much smaller. A similar trend can be seen in the computational study by Di Tommaso and Decleva [2] in the C 1s β parameters of fluoroacetylene (FCCH) and 1,1-difluoroethene (F_2CCH_2). The asymmetry parameter is lower for the fluorinated C and, in FCCH, approaches faster the β value for the non-fluorinated C than in F_2CCH_2 . In our case the effect of the substitution is particularly marked in the low energy region, where a large steep decrease towards threshold is observed for the C 1s β parameter of the substituted

FIG. 4. Photoelectron asymmetry parameters in $\text{CH}_3\text{CH}_2\text{Cl}$, CH_3CHCl_2 , and CH_3CCl_3 of a) chlorinated b) methyl C $1s$. A discussion of the error analysis is provided in [8].

carbon. A somewhat weaker but consistent effect is also observed for the C $1s$ β of the methyl group, which gradually approaches the β of ethane when the degree of Cl substitution is decreased. Theoretical and experimental data are in generally good agreement, although the calculated values are systematically lower than the experimental ones. At higher energies the methyl C β shows a monotonic increase, while the β parameters of the substituted carbon show noticeable oscillations in the calculated profiles, which become increasingly marked with increasing substitution. The oscillation period is close to that observed in the cross sections, so one can assign it to the same origin, the photoelectron diffraction. Unfortunately the experimental values are too sparse to reproduce this oscillatory effect. Even at the highest energy considered, the β parameters of the substituted carbon remain lower than those of the methyl carbon, and the β values follow the order $\text{CCl}_3 < \text{CHCl}_2 < \text{CH}_2\text{Cl} < \text{CH}_3$, as can be seen in Fig. 4.

In conclusion, using experimental and theoretical analysis, we have pointed out a pure molecular effect by demonstrating the importance of intramolecular scattering on the photoelectrons' angular distributions. We have shown that chemical substitution has a large effect on the β parameters. In particular, at the low photon energies the photoelectrons emitted from the substituted carbon are efficiently redirected from their trajectories by the scattering from the surrounding Cl atoms. The scattering effect is also observed in the β parameters of

the methyl group carbon, showing smaller but consistent modulations: the more halogenated the molecule is, the more β parameters deviate from their asymptotic values. The observations are supported by theoretical calculations making it possible to single out the various continuum channel contributions. The angularly resolved photoelectron spectroscopy in the laboratory frame is found to be a sensitive probe of the chemical environment, depending on intramolecular scattering effects even in randomly oriented molecules.

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