Interference Effects in the Valence Shell ionization of
Simple Hydrocarbons

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Abstract. Interference effects in the outer valence ionization cross sections have been theoretically investigated in simple hydrocarbons, and found comparable to those observed in core and inner valence ionizations. Notably short period oscillations give strong evidence of molecular orbital delocalization over the entire molecule. Also in the case of unresolved ionizations, interference patterns still survive in band ratios and convey useful information.

1. Introduction
Interference effects due to coherent emission from two equivalent atomic centers were predicted long ago by Cohen and Fano [1], and have been amply verified in recent studies. Actually most investigations have concentrated in the core region, because of the simple nature of relevant molecular orbitals (MO) $1\sigma_g$, $1\sigma_u$, which correspond to the symmetric and antisymmetric combinations of atomic 1s orbitals (AO). Experimentally their study requires resolution of the two individual ionization channels, because oscillations appear exactly out of phase in the two channels, and cancel in the unresolved cross section. In practice this restricts investigation to the N$_2$ [2, 3] and C$_2$H$_2$ [4, 5] molecules, which have a larger separation of about 100 meV because of the short interatomic distance, caused by the triple bond, just at the limits of experimental feasibility. In a recent study [6] we have considered the possibility of investigating the same phenomenon in the inner valence orbitals originating from the C2s AO, the relevant MOs being split by a few eV, and therefore easily investigated. This has allowed to consider interference in the three simplest hydrocarbons C$_2$H$_2$, C$_2$H$_4$ and C$_2$H$_6$, with the aim of investigating the expected dependence of interference pattern on the bond length. This was indeed observed, and it was shown that accurate theoretical simulation of the interference pattern is potentially able to recover the geometric information from the experimental data with high accuracy. It also turned out that the pattern was more complex, due to partial delocalization of the inner valence MOs on the full molecule, and to the presence of many-body effects, which in turn make the study of such structure a potential source of important information also about the electronic structure of the target. A full delocalization is expected in the outer valence shell, which could be expected to wash out completely the interference structure. On the other side, outer valence ionization is very rich, as it comprises several orbitals, including those most responsible for the bonding and chemical properties of the compound. Although in complex molecules the full valence spectrum may become very crowded and often unresolved, typically a few ionic states give rise to well resolved isolated bands, or even resolved composite bands can be analyzed, giving a wealth of opportunities for application. In order to investigate such possibility in this paper we report structures in the outer valence shell cross section of the same three molecules C$_2$H$_2$, C$_2$H$_4$ and
C$_2$H$_6$, and the more complex C$_3$H$_8$. All cross sections have been computed at the static density functional level, employing the LCAO B-spline approach previously developed, which has been shown to produce interference structures in excellent agreement with the experiment \cite{5, 6}. We refer to the literature for a description of the method \cite{5, 7, 8}.

2. Results and discussion

2.1. C$_2$H$_2$

In this case the outer valence shell only comprises two orbitals: the $3\sigma_g$ (HOMO) and the $1\pi_u$ (HOMO-1). $1\pi_u$, in a minimal LCAO picture, is purely localized on the two carbons, being composed of symmetric and antisymmetric combination of C2p orbitals, while the $3\sigma_g$ is fully delocalized and contains an important contribution from H 1s. The relevant cross section ratio is reported in Fig. 1. Despite the different nature, a very clear interference pattern emerges, indicating that it is mostly dominated by the different g, u symmetry of the two orbitals, and not by the details of their composition. The average cross section ratio is close to the statistical ratio of 0.5.

2.2. C$_2$H$_4$

In this case the outer valence shell comprises four different ionizations, $1b_{3u}$ (HOMO), $1b_{2g}$, $3a_g$, $1b_{2u}$, all well resolved, and an ample choice of cross section ratios to investigate. We have chosen the ratio of HOMO ($\pi$) to the three higher lying orbitals ($\sigma$), which are reported in Fig 2. Well developed interference patterns are apparent in all three ratios. The two peaks, around 70 and 400 eV, quite similar in all ratios, are therefore probably attributed to patterns in HOMO, while the profiles of the two ratios $1b_{3u}/1b_{3g}$ and $1b_{3u}/1b_{2u}$ show an additional relative oscillatory pattern, with smaller period. To see it more clearly, we have plotted the ratio $1b_{2u}/1b_{3g}$ in figure 2 where their structure appears very clearly. It is interesting that $1b_{2u}$ and $1b_{3g}$ have basically opposite composition, $1b_{2u}$ is 64% C2p$_y$ + 34% H1s, and the composition is reversed in $1b_{3g}$. These opposite parity, delocalized orbitals, extending over the whole molecule, originate the regular, short period interference pattern, that would be otherwise unexpected, given the single short C-C internuclear distance in C$_2$H$_4$. 

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{ratio.png}
\caption{3$\sigma_g$/1$\pi_u$ cross section ratio for C$_2$H$_2$}
\end{figure}
(a) $1b_{3u}$ (HOMO) versus $1b_{3g}$, $3a_g$, $1b_{2u}$ ionizations

(b) $1b_{3u}/1b_{3g}$ ratio

**Figure 2.** Cross section ratios for C$_2$H$_4$
2.3. $C_2H_6$

In this case, because of the higher symmetry, only three outer valence ionizations are present: $1e_{1g}$ (HOMO), $3a_g$ and $1e_{1u}$. We have considered HOMO/$3a_g$ and HOMO/$1e_{1u}$ cross section ratios reported in Fig. 3.

While the former displays well developed oscillations, the latter shows a flatter and less regular pattern, with shorter oscillation period, like in the $1b_{2u}/1b_{3g}$ case in $C_2H_4$, again a sign of the delocalized nature of the orbitals involved. So in this case, more than the $u/g$ difference, it is the specific nature of the MOs that dominates the pattern.

2.4. $C_3H_8$

This serves as an example of a congested outer valence region. There are seven ionizations, spanning 6-7 eV, which cannot be resolved, but give rise to three well separated composite bands I: $2b_2$, $6a_1$, $4b_1$; II: $1a_2$, $3b_2$; III: $5a_1$, $1b_1$ [9]. To give an idea of the complexity we have rather arbitrarily plotted (Fig. 4) the ratios of all cross sections relative to the $1a_2$ one, chosen because of its simple and localized nature, about 50% $C_2p_x$, 43% $1s$ on the terminal $CH_3$ groups.

One can observe a very regular oscillatory pattern in the $1b_1/1a_2$ ratio, together with many strong but irregular features. An alternative, experimentally feasible, is to consider ratios of the composite bands, which are also reported in Fig. 4. Although many details are lost, and interpretation may be more difficult, significant interference patterns still survive, and may yield sufficient information in combination with a theoretical simulation.

3. Conclusions

We have shown that well developed interference patterns emerge from cross section ratios in the outer valence shell of simple hydrocarbons. They contain important information both on the geometrical and electronic structure of the molecule. Strong evidence of the sensitivity of the
(a) Cross section ratio of all valence orbitals with respect to the 1a$_2$ ionization

(b) Ratios of the composite bands resolved in the outer valence spectrum, band 1 (2b$_2$, 6a$_1$, 4b$_1$), band 2 (1a$_2$, 3b$_2$), band 3 (5a$_1$, 1b$_1$)

Figure 4. Cross section ratio for C$_3$H$_8$
interference pattern to molecular orbital delocalization over the full molecular skeleton is given by oscillation period shorter than expected on the basis of C-C bond distance. Also in the case of unresolved ionizations, ratios of composite bands still show significant interference pattern and convey useful information.

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