

Single-Photon $K^{-1}K^{-1}$ Double Core Ionization of C_2H_{2n} ($n=1-3$) Sequence Molecules as a Potential New Tool for Chemical Analysis

Production of two-site double core-hole ($K^{-1}K^{-1}$) states has been studied for C_2H_{2n} ($n = 1-3$) molecular series by multi-electron coincidence spectroscopy to verify the theoretical prediction of larger chemical shift than in conventional single core-hole states. A comparison among the cross sections of $K^{-1}K^{-1}$ states formed for these molecules indicates that the knock-out process is predominant in the production of the $K^{-1}K^{-1}$ states.

Electron spectroscopy for chemical analysis (ESCA) [1] is a very powerful analytical method relying on the chemical shift that reflects the environment of a given atom in a molecule. For hydrocarbon molecules this shift is generally very small, but Cederbaum et al. predicted in 1986 [2] that, in C_2H_{2n} ($n = 1-3$) molecules, the two-site double core-hole states ($K^{-1}K^{-1}$) show a much stronger effect than in single core-hole (K^{-1}) states. Therefore, we systematically studied the production of the $K^{-1}K^{-1}$ states for C_2H_2 , C_2H_4 and C_2H_6 to verify the prediction [3]. In the past few years, much attention has been paid on the formation of the double core-hole (DCH) states in molecules with the advent of X-ray Free Electron Laser (X-FEL), which offers the possibility of creating DCHs in a two-photon process [4]. However, the present self-amplified spontaneous emission operation mode of XFELs results in low photon resolution, and is not always sufficient for the abovementioned present purpose.

The experiments were carried out at the undulator beamline BL-16A in single bunch top-up mode by multi-electron coincidence spectroscopy, where we developed a magnetic bottle analyzer with high collection efficiency to detect all the electrons in coincidence and to resolve them in terms of energy through multiple photoionization processes [5].

In Fig. 1, we plot the number of coincidence events as a function of the binding energy (BE) of the DCH states: $BE = h\nu - (E_{ph1} + E_{ph2})$ where $E_{ph1} + E_{ph2}$ is the sum of the energies of the two photoelectrons. We

observe clearly the one-site DCH (K^{-2}) states and also satellite peaks ($K^{-2}V^{-1}V'$) where a valence electron from orbital V is excited simultaneously to a vacant orbital V' . The most important result, the production of the $K^{-1}K^{-1}$ states, can be perceived as small peaks at BE 590-600 eV. The experimental binding energies of the $K^{-1}K^{-1}$ states are 596.0 ± 0.5 eV, 593.3 ± 0.5 and 590.2 ± 0.5 eV, respectively, for C_2H_2 , C_2H_4 and C_2H_6 . This observation can be compared to the BE of K^{-1} states for these three molecules, of which the chemical shift is at most 0.5 eV, and is considered to verify the abovementioned prediction. It should also be mentioned that the density-functional theory calculations shown by the vertical arrows reproduce the experimental observations quite well [3].

The branching ratios of $K^{-1}K^{-1}/K^{-1}$ can be obtained from the peak intensities in Fig. 1, and were found to be 2.0×10^{-5} , 1.34×10^{-5} and 1.26×10^{-5} for C_2H_2 , C_2H_4 and C_2H_6 , respectively. This systematic decrease of the ratios along the C_2H_{2n} sequence approximately scales as the inverse square of the C-C bond length (C=C: 1.2 Å, C=C: 1.34 Å, C-C: 1.54 Å). This is a strong indication that the double site ionization process is predominantly caused by the knock-out mechanism, where the primary photoionized electron collides with a K-shell electron in the neighboring atomic site, which can escape the molecular field with the primary electron. It should be emphasized that this study was made possible thanks to the high performance and very stable single-bunch top-up mode operation at the 2.5-GeV PF ring.

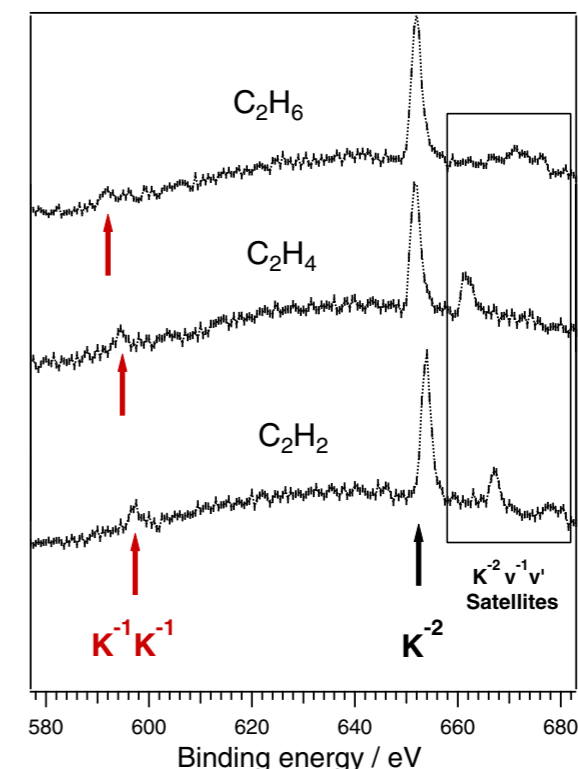


Figure 1: Spectroscopy of $K^{-1}K^{-1}$ double core-hole states of the C_2H_{2n} sequence molecules.

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