Evidence of Single-Photon Two-Site Core Double Ionization of C_2H_2 Molecules

We present the first experimental evidence of molecular $K^{-1}K^{-1}$ states, where two K shell electrons are removed from two different atoms of the molecule. These states were produced by single photon double ionization, an extremely weak process that relies on electron correlation and is reasonably well described by an internal collision process. This proof-of-principle experiment opens up the way to establishing the spectroscopy of double core hole states (DCHs), which would overcome some limitations of the traditional ESCA technique (Electron Spectroscopy for Chemical Analysis), as discussed previously from a theoretical point of view.

Interest in DCHs was expressed 26 years ago by Cederbaum et al. [1], who predicted that $K^{-1}K^{-1}$ spectroscopy would distinguish the C_2H_{2n} series (n = 1, 2 and 3), while it was impossible to determine the nature of the C-C bond from traditional ESCA (K^{-1} spectroscopy). Theoretical interest revived recently [2] with the advent of X-ray free electron lasers (XFELs), which offer the possibility of creating DCHs in a two-photon process. Theory showed that DCHs spectroscopy gives direct access to the relaxation energy, a property of the final state. K^{-2} states, where two K shell electrons are missing from the same atom, have recently been observed both on XFELs [3] and on synchrotrons [4]. We present here the first evidence of $K^{-1}K^{-1}$ states formed by synchrotron radiation [5].

The experiments were carried out at the undulator beamline BL-16A in a single bunch top-up mode and used the magnetic bottle analyzer developed by the group of Professor K. Ito.

The process under study is shown schematically in Fig. 1: $K^{-1}K^{-1}$ states are populated by single photon core double ionization. These excited states then decay by the sequential Auger decay of each core hole, releasing two Auger electrons of close energies, in the 200–250 eV range. Because of the dead time of our detector, these two Auger electrons are not distinguished in our experiment, and we searched for the weak $K^{-1}K^{-1}$ signal in the three-electron coincidence events which include detection of one such Auger electron. Figure 2(a) shows the energy correlation between the two other coincident electrons. It reveals a weak diagonal line associated with the formation of $K^{-1}K^{-1}$ states (red arrow), together with the more intense diagonal lines (green arrow) due to the formation of K^{-2} states. The projection in Fig. 2(b) of the two-dimensional map onto the x=y diagonal reveals clearly the peaks associated with the $K^{-1}K^{-1}$ and K^{-2} states, from which their binding energies can be retrieved. As shown in Fig. 2(c), the K^{-2} states are more clearly revealed in four-electron coincidences where both released Auger electrons with well separated energies are detected. This part is similar to our previous work on the isoelectronic N_2 molecule [4].

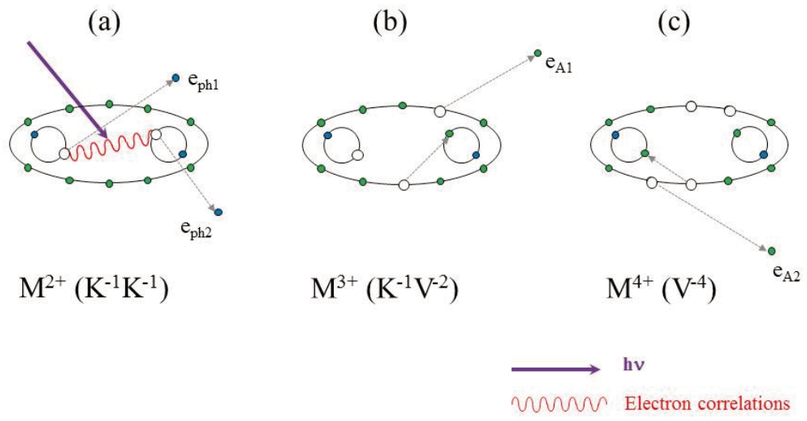

Figure 1
Schematic representation of the process studied here: single photon core double ionization creates a $K^{-1}K^{-1}$ state (a). This is followed by the sequential Auger decay of each core hole, populating first a $K^{-1}V^{-2}$ state (b) and then a V^{-4} one (c) (where V designates a valence shell).

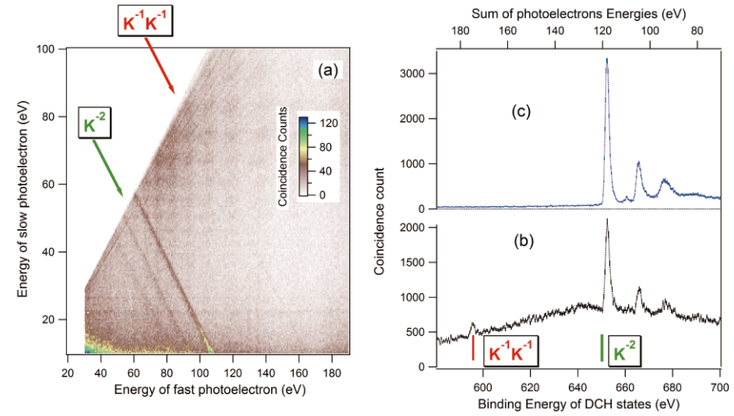

Figure 2
(a) Energy correlation map for the two photoelectrons emitted upon core double photoionization of the C_2H_2 molecule. All events considered here imply the coincidence detection of three electrons, one of them having an energy in the 230–250 eV range. (b) Histogram of the sum of the energies of the two photoelectrons, deduced from (a) integration along the diagonal lines. (c) Similar to (b), but the coincidence events imply here detection of four electrons, of which two each are in the 200–270 eV and 270-320 eV ranges. A photon energy of 770.5 eV was used.

From the number of coincidence events and taking into account the measured detection efficiencies, we estimated the relative probability P to create $K^{-1}K^{-1}$ states rather than K^{-2} states, that is, the ratio of the probability of extracting two K-shell electrons each from a different C atom to the probability that they are extracted from the same C atom. One obtains P = 1.6 ± 0.4%. The two-site K-shell double ionization process is reasonably well described by a simple internal collision model (knock-out) in which an initially ionized K shell electron collides and ejects a second K-shell electron from the neighboring atom. The model for the single-site K-shell double ionization process includes also the contribution from the shake-off mechanism. The resulting prediction of P = 3.2% [5] is in reasonable agreement with experiments.

Our work demonstrates that, in spite of the very low single-photon core double ionization probabilities, it is possible by this method to establish the spectroscopy of DCHs states, and even of the potentially more interesting $K^{-1}K^{-1}$ ones; we are currently exploring this subject. Our approach is also a relatively cheap alternative way of obtaining DCHs spectroscopic data without relying on two-photon absorption processes triggered by a XFEL source [6]. Our method seems also to be more precise and more selective, due to the multi-coincidence techniques that we use.

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