



Single-photon double and triple ionization of acetaldehyde (ethanal) studied by multi-electron coincidence spectroscopy



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ABSTRACT

Single-photon multiple ionization processes of acetaldehyde (ethanal) have been experimentally investigated by utilizing a multi-particle coincidence technique based on the time-of-flight magnetic bottle principle, in combination with either a synchrotron radiation source or a pulsed helium discharge lamp. The processes investigated include double and triple ionization in the valence region as well as single and double Auger decay of core-ionized acetaldehyde. The latter are studied site-selectively for chemically different carbon core vacancies, scrutinizing early theoretical predictions specifically made for the case of acetaldehyde. Moreover, Auger processes in shake-up and core-valence ionized states are investigated. In the cases where the processes involve simultaneous emission of two electrons, the distributions of the energy sharing are presented, emphasizing either the knock-out or shake-off mechanism.

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1. Introduction

Experimental single photon double ionization studies of atoms and molecules were carried out already at the end of the 1960s and onwards in form of Auger electron spectroscopy of atoms and molecules [1–7], often augmented by theoretical investigations [3,5,8,9]. The majority of these investigations were performed using electrostatic hemispherical electron energy analyzers which provide relatively high resolution, but which detect electrons only within comparatively small kinetic energy ranges and with limited capability to obtain information on the inherent energy correlation of the emitted electrons.

Double photoionization electron coincidence spectroscopy based on a magnetic bottle introduced by Eland et al. [10] in 2003 opened up the possibility to determine the correlation of electrons with a wide range of kinetic energies. To begin with, this method was used to study valence double ionization of atoms and molecules using a pulsed He lamp [10–18] or synchrotron radiation [19], and was subsequently applied to studies of core-valence double photoionization of atoms and molecules [20–26] utilizing

X-radiation. Both processes are examples of double ionization, where the two electrons emitted may share the excess energy provided by the absorbed photon arbitrarily, in contrast to fixed electron kinetic energies typically observed in cases of single core shell ionization followed by normal Auger decay. This method was successfully expanded to the study of valence triple ionization [27,28], where the excess photon energy is shared between three emitted electrons, and to the case of double Auger decay [27–30] of a single core vacancy.

Acetaldehyde is an organic compound denoted chemically as CH₃CHO. Its electron configuration in the neutral ground state can be expressed as:

$$\text{core } (4a')^2(5a')^2(6a')^2(7a')^2(1a'')^2(8a')^2(9a')^2(2a'')^2(10a'')^2$$

where the three core orbitals 1a', 2a' and 3a' are localized on the oxygen and two different carbon atoms. Those orbitals are essentially atomic-like [31] and are therefore referred to as O1s and C1s orbitals in what follows.

From previous work (see e.g. Refs. [32,33]) it is known that compounds with two core orbitals localized on atoms of the same element, but in different chemical environments, may demonstrate different properties in the Auger processes depending on the core orbital involved. Acetaldehyde is interesting in this respect as it contains one carbon atom in a methylic group and another carbon

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atom in a formyl group. This offers the possibility of site-specific investigations of photoionization processes which involve the core orbitals, such as single and double Auger decay. The single ionization valence photoelectron spectrum of acetaldehyde was reported in the mid 1970s by Chadwick et al. [34], Tam et al. [35] and Kimura et al. [36] with the outermost valence cationic state located at 10.231 eV ionization energy [37]. Experimental studies of the ion fragmentation of acetaldehyde in coincidence with photoelectrons were presented in 1977 by Golovin et al. [38] and in 1982 by Johnson et al. [39]. Subsequently, Keane et al. [37] published in 1991 a study on the shake-up spectrum of this molecule. The same year Correia et al. [40] carried out an experimental and theoretical study of the normal Auger decay spectra of acetaldehyde with precise measurements of the core ionization energies. According to their work, the O1s ionization energy is 538.64 eV, and the formyllic C1s and methylic C1s ionization energies are 294.45 eV and 291.80 eV, respectively. A more thorough assignment of the Auger spectra was presented in 1995 by Minelli et al. [41].

In this work we report on a new experimental study of single-photon multiple ionization of acetaldehyde using a magnetic bottle multi-electron correlation spectrometer and compare our results, where possible, with existing theoretical predictions as well as previous experimental studies. In particular we present the valence double ionization electron spectrum of acetaldehyde in comparison with the known spectrum of normal Auger decay associated with the O1s core hole. This comparison gives us the possibility to assign the features observed in the valence double ionization electron spectrum.

In order to investigate site-specific effects we examine the single and double Auger spectra which are extracted by selecting events corresponding to a specific core-electron energy. In the case of single Auger decay we scrutinize the early theoretical predictions of Minelli et al. [41] which so far lacked comparison to suitably extracted experimental spectra. Selecting on the energy of the ejected electron(s) also allows us to investigate the fate of more exotic states such as shake-up and core-valence (sometimes called “shake-off”) states. In particular, we compare the Auger decay of the shake-up states with the Auger decay of the ground state of the core ionized species. Similarly, the triple valence photoionization route is compared with both the double Auger decay of the core-ionized molecule and the Auger decay of core-valence doubly ionized acetaldehyde, since all three processes can lead to the same triply ionized final states.

2. Experimental and analysis details

The experiments were performed utilizing a versatile multi-electron coincidence technique based on a time-of-flight magnetic bottle spectrometer [10]. A key asset of this technique is the capability to reveal the energy correlation of multiple electrons originating from the same photoionization event. Electrons created in the light-matter interaction region of the spectrometer are guided by a combination of a strong and weak magnetic field [42] through a flight tube of about 2 m length towards a multi-channel plate (MCP) detector with multi-hit capability.

The majority of the experiments were carried out at beam line U49/2 PGM-1 of the synchrotron radiation facility BESSY-II at the Helmholtz Zentrum, Berlin. The storage ring was operated in single bunch mode providing 30 ps long light pulses at a repetition rate of about 1.25 MHz. In order to reduce the X-ray pulse repetition rate further to a level adequate for unambiguous time referencing of our set-up, a mechanical chopper [43] was used, synchronized to the radio frequency signal of the storage ring. The experimental runs were carried out at the photon energies of 95 eV, 350 eV and 600 eV. Depending on the photon flux, the energy resolution

of the monochromator was chosen to be about 300 meV or better. In addition, we carried out auxiliary measurements in our home laboratory using a pulsed helium discharge lamp at the photon energies of 21.2 eV (He-I α) and 40.8 eV (He-II α).

The vapor pressure of acetaldehyde at room temperature is sufficiently high to create a suitable sample gas pressure in the spectrometer without the need for additional heating. We used a commercially available sample with a stated purity >99% and used several freeze–pump–thaw cycles in order to remove air and other impurities. In order to verify the purity, we recorded conventional photoelectron spectra both in the valence and core regions and compared them to the reference spectra known from the literature [34–37,39].

For the synchrotron radiation experiments, the Argon L₂ and L₃ photoelectron lines [44] as well as the core ionization energies of acetaldehyde known from the literature [40] were used to calibrate the flight time to kinetic energy conversion. For the helium lamp experiments the valence photoelectron spectrum of oxygen recorded at 21.2 eV [45] and the valence photoelectron spectrum of acetaldehyde itself [36] were used for calibration purposes. The photon energy of 95 eV is sufficient for double photoionization involving all valence orbitals, but not core orbitals, while 350 eV and 600 eV photons induce processes involving the core orbitals of carbon and oxygen atoms, respectively. Thus, our analysis of processes involving the formation of carbon holes (both formyllic and methylic) is based on the 350 eV run, while for processes involving the oxygen electron, we used the data taken at the photon energy of 600 eV.

The time-of-flight to kinetic energy conversion is based on

$$E_{kin} = \frac{D^2}{(t - t_0)^2} + E_0 \quad (1)$$

where t denotes the measured flight time and E_{kin} the electron kinetic energy, and where D (which contains the length of the flight path), t_0 and E_0 are calibration parameters derived by least-square fitting of the features measured in the calibration spectra in comparison to the reference spectra.

The time resolution or bin size of the analog-to-digital converter was set to 100 ps. Because of the non-linearity of the conversion formula, the spectra and coincidence maps directly transformed to the energy scale would have non-constant bin size. In order avoid distortion of the intensity distributions, we have chosen a constant bin size of 0.2–1.0 eV (depending on the statistics and resolution in the particular cases) and redistributed the intensities on the basis of the degree of overlap between constant and non-constant bins. Thus, one electron can contribute to several neighboring bins conserving the sum of the proportions. The resulting coincidence maps have electron kinetic energies on their axes. In order to obtain the double and triple ionization energy scales used in Figs. 1 and 8, and in Figs. 6 and 10, respectively, we changed the representation of the map to have the summed electron energies on one of the axes and then project the data onto this axis. The resulting spectrum then can be easily converted to the double or triple ionization energy scale by taking into account the photon energy used. The double ionization energy scale of the Auger electron spectra shown in Figs. 4 and 5 below, has been established by subtracting the kinetic energy of the Auger electron from the associated 1s ionization energy.

In the case of the double Auger process (see Fig. 6 below), we have selected triple coincidence events, where one of the electrons has the kinetic energy of the core electron of interest and where the kinetic energies of two other electrons fall outside this energy range. Then similarly to the single Auger case, the triple ionization energy scale of Auger pairs has been derived as the kinetic energy sum of electron pairs relative to the lowest single core ionization

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