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Homonuclear Site-Specific Photochemistry by an Ion-Electron Multi-Coincidence Spectroscopy Technique

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Abstract

By combining multi-particle coincidence detection of electrons and ions with ionization by soft X-ray synchrotron radiation we demonstrate an effective tool for atomic spectroscopy and site-specific photochemistry. Its most novel capability is application to molecular fragmentation after *K*-shell vacancy production in atoms distinguished only by their chemical environment.

INTRODUCTION

Site-specific photochemistry was initiated in the 1980's by Eberhardt and coworkers [1, 2] using tuneable soft X-rays to produce inner shell excited states, and detecting ionic fragmentation products in coincidence with single Auger electrons. Closely related techniques were later extended to a range of molecular targets, starting with halocarbons and zero-valent metal complexes by several teams [3–8]. In all these later works with the exception of that of de Brito *et al.* [6, 7] on ozone, site-specific excitations were created at atoms of different elements in the target molecules; detection of a single Auger electron then identifies the atom and also determines the energy deposited in the final singly-ionized state. More recently coincidence apparatus which also allows determination of the angular distributions of both particles has been developed and applied [9, 10]. Important early work on selective bond breaking was carried out in Hanson's group in the USA [11–13] which was followed up by Morin *et al.* [14] and extended by Simon's group [15, 16] in France. The most recent work in the field has been done in Japan by Ueda's group [17–19] and Kukkk's group in Finland [20, 21].

Site-selective fragmentation can possibly arise in two ways; first nuclear motion local to the core-hole site could commence immediately on ionization and proceed to some extent before the hole is filled in the Auger effect. The magnitude of this effect will depend on the mean lifetime of the core hole and on the strength and nature of the original bonding. A largely electrovalent bond, for instance, will lose almost all its binding power if a core electron is removed from the anionic atom. We can also expect this effect to be stronger for double core holes (*cf.* Refs. [22–26] and references therein) than for single holes, and to be especially strong for two-site double core holes (*cf.* Refs. [27–30]) because of the coulomb repulsion. Secondly, the electrons taking part in the Auger effect come from orbitals with greatest density at the core-hole site; generally the bond weakening upon their loss will also be located in the same vicinity. The localisation of ion internal energy around the core-hole site is opposed by the strong tendency of all internal energy in molecular ions to become statistically distributed before fragmentation, as is notably confirmed by the wide success of the quasi-equilibrium theory of mass spectrometry [31]. Because of this internal energy randomisation, site-selection effects in cations are generally rather small. By contrast, a 100% effect has recently been found in a core-excited anion [32].

In this work we use detection of ionic fragments in coincidence with two or more electrons to select both the initial excitation site and the energy deposited in doubly charged ions, which generally dissociate very rapidly, hopefully before internal energy randomisation. Key to the technique is the use of a magnetic bottle time-of-flight (TOF) electron spectrometer with added ion detection capability [33], in a configuration different from the one developed earlier by some of us [34, 35]. The new configuration gives very high collection efficiency for both electrons and thermal ions, making coincidence measurements particularly favourable. The ionizing radiation is monochromatised synchrotron light from a storage ring operated in single bunch mode. Because the inter-pulse period is much shorter than the ion time of flight, a second key component is a newly developed synchronous chopper to extend the pulse interval from about 1 to about 80 microseconds [36].

EXPERIMENTAL METHOD AND APPARATUS PERFORMANCE

Because the basic magnetic bottle TOF electron spectrometer has been fully described before [37], we concentrate here on the modifications used for effective detection of ions in coincidence with the electrons. The modified layout and electronic circuit is indicated in Fig. 1. An inner flight tube, isolated from ground, allows electrons to be retarded and ions accelerated. Its opening next to the ionization region is equipped with an aperture smaller than the overall tube diameter, which reduces penetration of the pulsed ion repeller field into the electron flight path. A positive pulse of 4 kV is applied after a brief delay from the ionizing light pulse to the permanent magnet, which is fitted with a flat front plate to provide a roughly uniform field over a laterally extended region. This pulse accelerates positive ions to a high enough energy to be registered at the usual multi-channel-plate electron detector without any change of working conditions. In operation the delay between arrival of a light pulse from the chopper and application of the repeller voltage is tuned to be as short as possible (a few 100 ns to 1 μ s) without disturbing the observed signal from electrons of the lowest energy of interest. Under these conditions, measurements on the atomic rare gases allowed determination of the collection/detection efficiency for electrons as 49% and for thermal ions as 31%. The numerical resolution for electrons was about 50, as usual, and the mass resolution for thermal ions was about 40, defined as full-width-half-maximum (FWHM); this low resolution was caused by the spatial extent of the ionization

zone in the direction of the field and is expected to be much better with a more point-like source. Because of the length of the 2 m flight path coupled with the small size (40 mm diameter) of the detector, the collection efficiency for ions of high kinetic energy such as charge-separation fragments from molecular double ionization is very much reduced. In practice such fragments are hardly detected at all. The high collection efficiency for electrons of all energies of interest means that multi-electron coincidences are recorded efficiently, as the results demonstrate. But the lack of high kinetic energy ions means that very few ion-ion coincidences from dissociation of multiply charged molecules are seen.

RESULTS

Atomic spectra

Some advantages of coincident ion detection in multi-electron spectroscopy of atomic ions were already rehearsed in a previous publication [38], in connection with our original, pulsed lamp-based technique which made use of two different detectors located at opposing ends of the flight time spectrometer [34, 35]. Besides unambiguous identification of the ionizing light pulse [38], which is now also provided for our synchrotron-radiation-based experiments by a mechanical chopper [36], another main advantage is the reduction in background noise caused by overlapping secondary electrons. The present technique provides the same advantages in a much more convenient form. It allows spectra of individual components to be extracted from measurements on mixtures of gases, which was impossible in the previous technique [38] where the apparatus had to be tuned to detect a single mass at a time. To illustrate this we show in Fig. 2 the spectra of doubly and triply ionized Ar at 100 eV, taken from a mixture of rare gases including both Kr and Xe, whose ionization cross sections are much greater than those of Ar at this photon energy. For Kr in a similar mixture, Fig. 3 contrasts the spectra of Kr^{2+} and Kr^{3+} populated by resonant Auger and simple Auger effects involving the same initial core vacancy.

Site-selective photochemistry

The crucial advance made by the present technique over previous experiments in site-selective photochemistry is that it allows selective excitation at atomic sites of the same

element in different chemical environments, retaining control of the energy deposited in the ions produced. Most significantly, this makes it possible to select distinguishable carbon atoms in a vast range of organic molecules. Despite its insensitivity to high energy ions, the technique in its present form produces quite rich mass spectra, which can be selected according to the energy of one, two or three photoelectrons emitted in the ionization. A simple test for site selectivity is to plot the spectra of the photolines, which are distinguishable by the shifts in energy caused by their different chemical environments, as coincident with different dissociation products. Fig. 4 shows the C1s photolines of acetone coincident with three of the major fragment ions. The relative intensities of the lines are close to 2:1 in favour of the CH₃ carbon atom when taken in coincidence with the ions C₃H₅O⁺, CH₃⁺ and CO⁺, for whose production as low energy fragments site-specific core ionization is apparently not important. But for the CH₃CO⁺ ion the coincident intensity is much lower when the -CO- carbon atom is the initial ionization site. This is clearly a site-specific effect whose exact mechanism will require further research. In a similar plot for the four distinguishable carbon atom sites in ethyl trifluoroacetate (see Fig. 5) we see more widespread selectivity; in particular the CF₃ group is progressively more fragmented, first to CF₂⁺ then to CF⁺ as the initial ionization site approaches more closely to the fluorinated end of the molecule. The intact low energy CF₃⁺ ion is actually most abundant when the core ionization site is at the further end of the molecule.

The site-selective fragmentation evident from plots of the photoline intensities is an overall effect, which integrates over all the energies and even the numbers of electrons ejected. Because multiple electrons are detected in this technique, we can examine the fragmentation processes in greater detail. The major process going on is Auger decay, which produces doubly charged ions. Fig. 6, a two dimensional map showing mass spectra against double ionization energy ($h\nu - E_1 - E_2$), reminds us that by far the most important factor determining the outcome of molecular fragmentation is the amount of energy deposited in the molecule or ion, as has been pointed out in previous studies of site selectivity [4]. The identity of the particular electronic state populated may also influence fragmentation behaviour, but we believe that this is a major effect only in very small molecules. For instance in Fig. 6, within each group of ions of similar mass, the dominant mass number decreases when the energy increases as more and more hydrogen is evaporated away as atoms or ions. At the highest energies, bare carbon groups, C⁺, C₂⁺ and C₃⁺ remain. For a given initial core hole,

the spectrum of energy deposition in the doubly charged ions is given by the Auger electron spectrum. Fig. 7 shows that the Auger spectra from holes at the two distinguishable C sites in acetone are distinctly different. That the same is true of ethyl trifluoroacetate has been observed in a separate experiment by Iwayama *et al.* [39]. It could be that the overall site-selective effects seen in Figs. 4 and 5 are entirely due to such differences in Auger spectra and thus to differences in energy deposition, rather than reflecting any real localisation of the excitation. To clarify this, we can compare mass spectra taken in coincidence with photoelectrons from specific sites and also with Auger electrons depositing the same initial energies in the doubly ionized products. Such mass spectra, from ionization at specific sites and depositing equal and relatively low (0-5 eV) internal energy in double ionization of ethyl trifluoroacetate are shown in Fig. 8. Despite the very poor statistics and low mass resolution, the spectra clearly show real localisation effects. Low-energy CH_3^+ ions are most abundant when the core hole starts on the CH_3 moiety, and there acetyl and (probably) ethyl ions are also produced as low-energy species. From the carbonyl carbon core site we see low energy CH_3^+ and CF_3^+ in about equal abundance, and (probably) some CO^+ . From initial core hole creation on the CF_3 carbon atom the only low energy fragment produced in any quantity is CF_3^+ itself. In addition to site and binding-energy specific double ionization by the Auger effect, this technique also allows similar studies of triple ionization by double Auger decay. We have investigated this briefly, and the triple ionization mass spectra produced from the two compounds studied here closely resemble those from double ionization at high binding energy.

Future developments

The experiments reported here represent a proof-of-principle, and were carried out in limited run time at a storage ring in the relatively scarce single-bunch mode. The synchronous chopper which we recently reported [36] will enable such work at storage rings operating in the soon-to-be more abundantly available hybrid modes. The spectrometer itself has been tested without any lateral focussing for ions of high initial kinetic energy, and without two-field time focussing [40]. These two straightforward and well-understood improvements will provide higher collection efficiency and much better mass resolution for ions, together with a capability to determine ion kinetic energy releases. The conveniently accessible mass range

will be extended by improved timing and an increase in the pulsed repeller field amplitude.

CONCLUSIONS

This magnetic bottle TOF technique for multi-particle photoelectron-photoion coincidence spectroscopy combines very high collection efficiency for electrons with high collection efficiency for thermal ions at useful resolution. It already opens up new vistas in the extension of site-specific photochemistry by inner-shell excitation to a whole range of carbon compounds. Improvements to the technique to enhance its resolution and sensitivity to high energy product ions can be confidently expected, and may possibly convert it into a useful tool for some particular tasks in molecular structure determination. This prediction will become most susceptible of realisation if problems of low cross-section can be overcome sufficiently for the technique to be used on fragmentation following double core-hole formation. Such investigations should be attempted soon for compounds of second row and heavier elements, where double core hole formation by, for instance, KLL Auger decay is a naturally high probability process.

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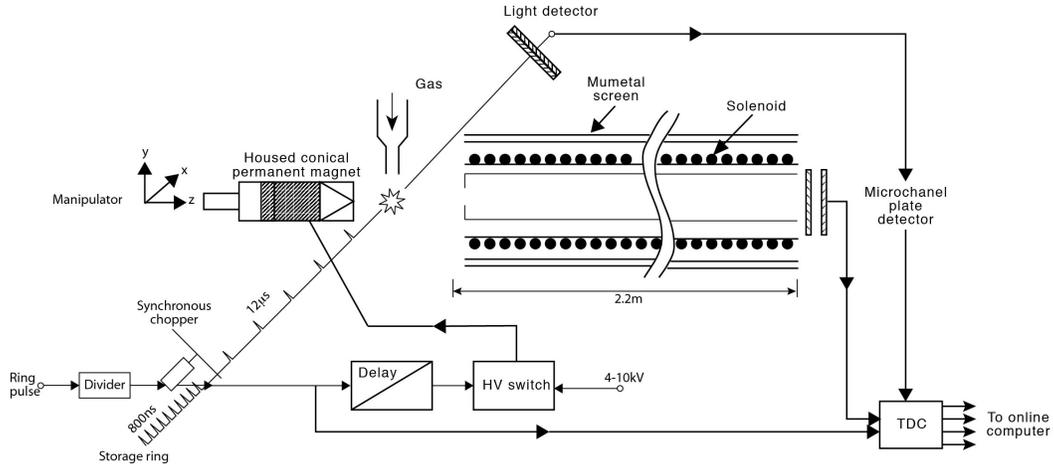


FIG. 1. Essential components of the magnetic bottle TOF apparatus to convert it into a multi-coincidence electron-ion spectrometer. The delay before the ion repeller pulse is set to the minimum possible without disturbing the slowest electrons of interest. Distances in the source region are 5 mm from magnet to ionization point and 7.5 mm from ionization to the aperture.

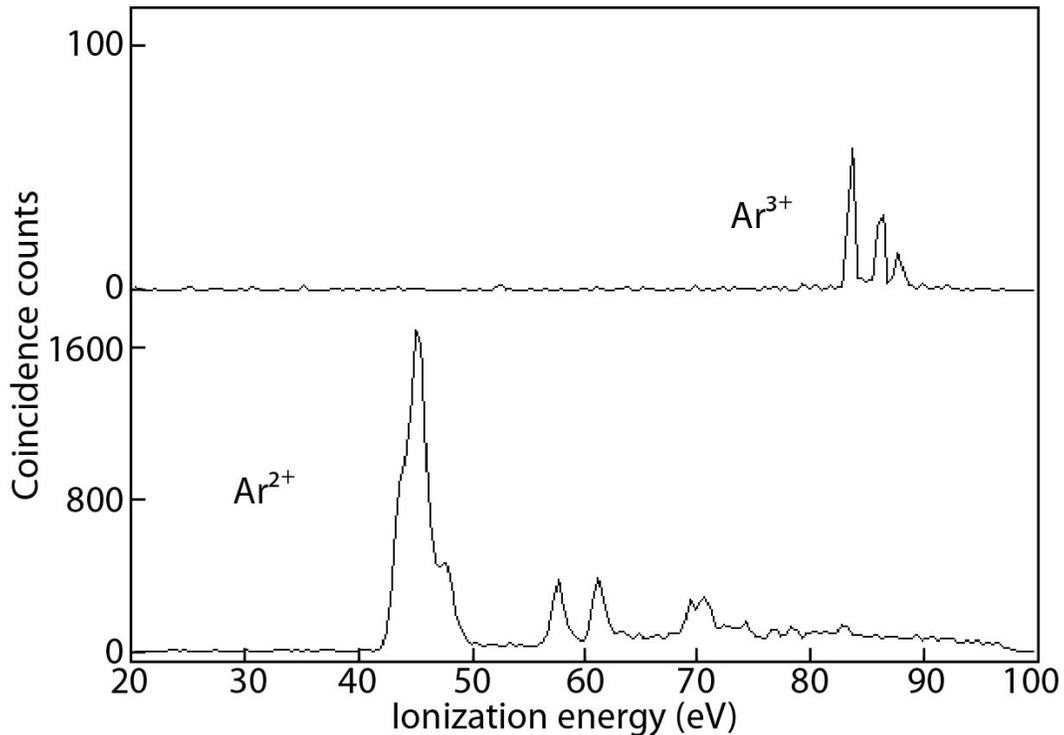


FIG. 2. Spectra of doubly and triply ionized argon from photoionization at 100 eV photon energy, below the inner shells. The spectrum of Ar^{2+} comes from threefold coincidences (1 ion, 2 electrons) and that of Ar^{3+} required fourfold coincidences.

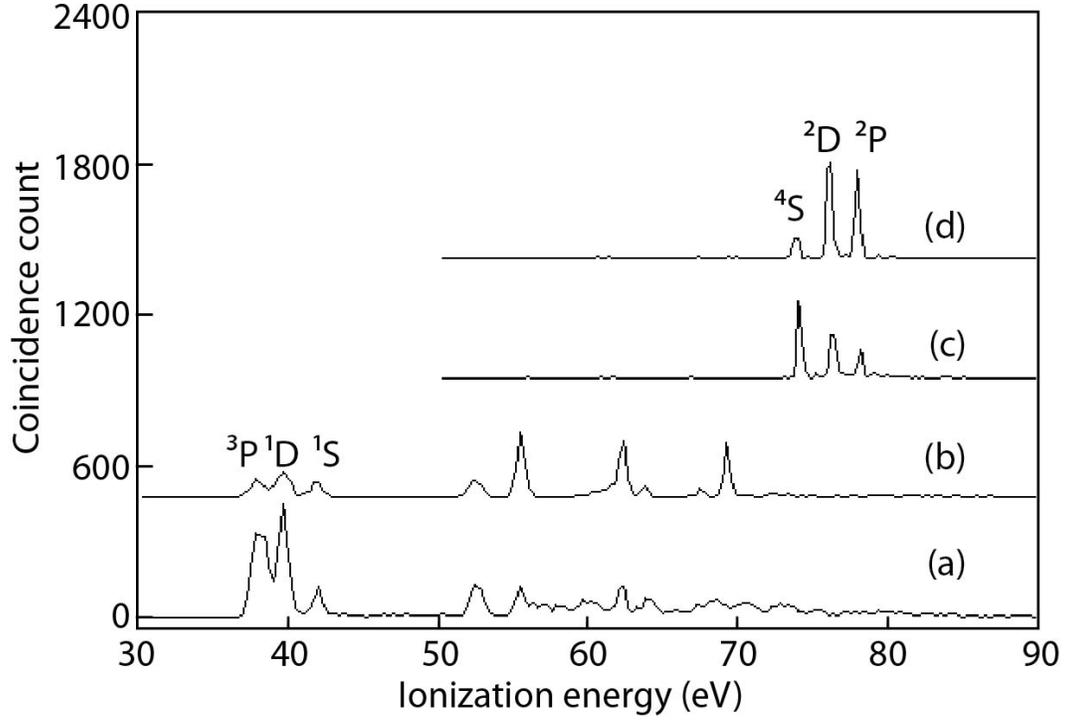


FIG. 3. Spectra of ionized krypton: (a) double ionization by resonant double Auger decay of the $5/2\text{-p}^*$ resonance at 91.2 eV; (b) double ionization from simple Auger decay of the $2\text{D}_{5/2}$ core hole state; (c) triple ionization by resonant triple Auger from the same resonance as in (a); (d) triple ionization by double Auger decay of the $2\text{D}_{5/2}$ core hole state. The double ionization spectra are from threefold coincidences and the triple ionization spectra from fourfold coincidences, as in Fig. 2.

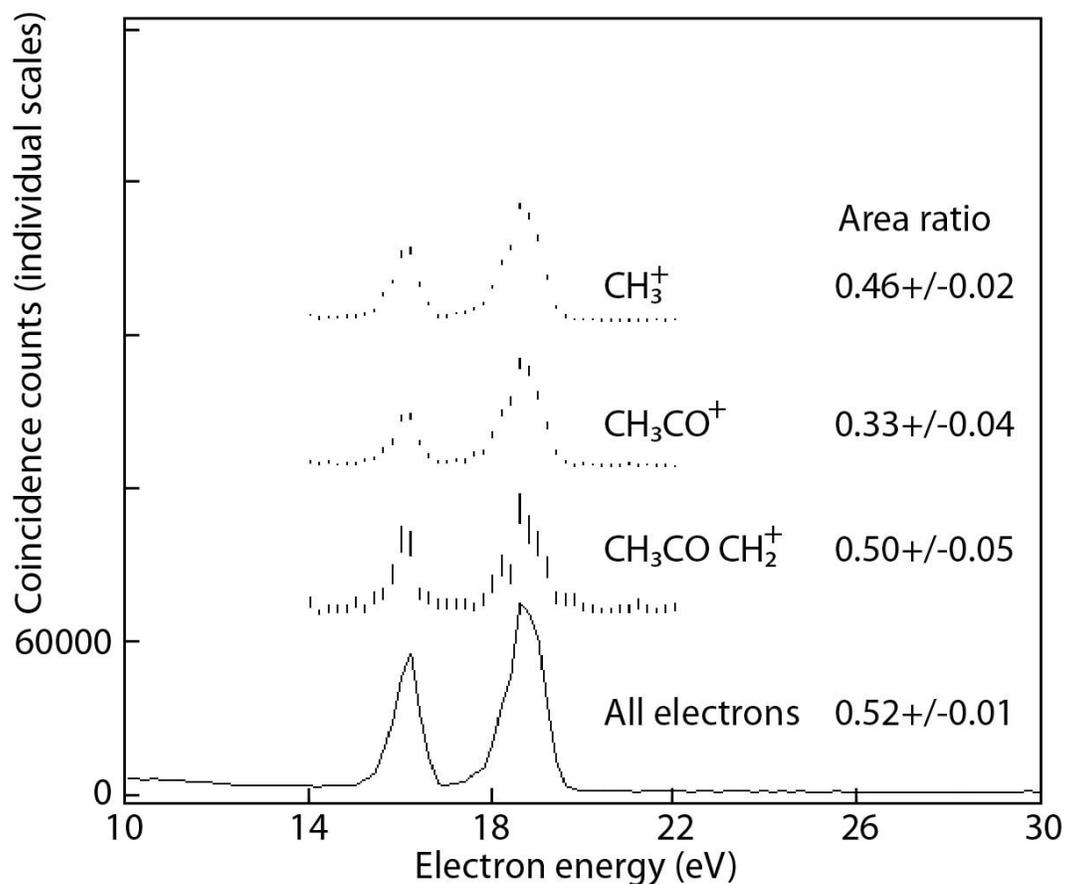


FIG. 4. Photoelectron spectra showing the C1s ionizations of acetone at 310 eV photon energy for all electrons and in coincidence with different low-energy ions. The area ratios given in the figure have been derived by summing the peak areas over exactly the same energy ranges in all cases, without background correction or allowance for the visible PCI distortion. They are given only for comparison amongst themselves and should not to be taken as absolute values.

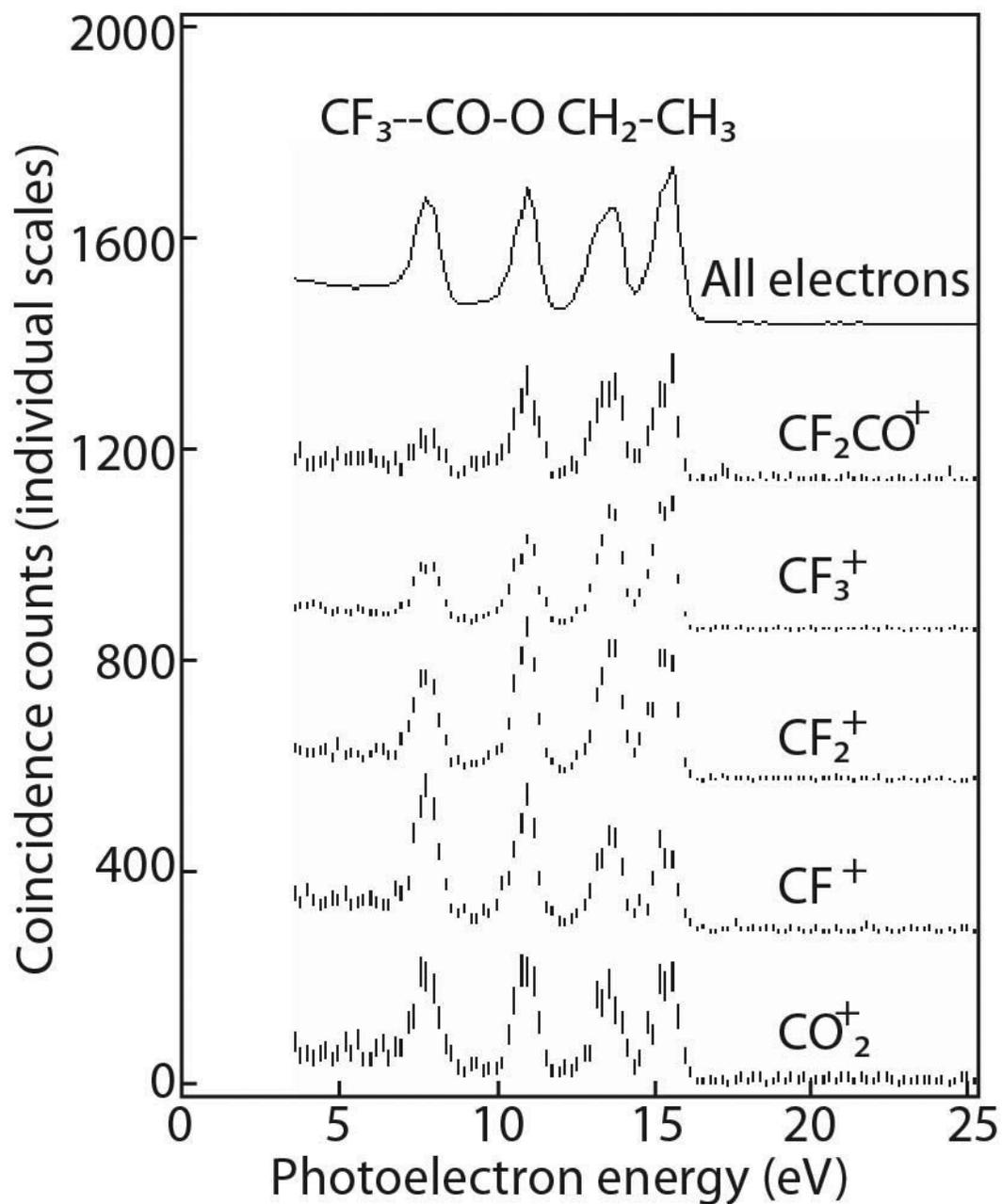


FIG. 5. Photoelectron spectra of the C1s orbitals in ethyl trifluoroacetate for all electrons and coincident with selected ions at 307 eV photon energy.

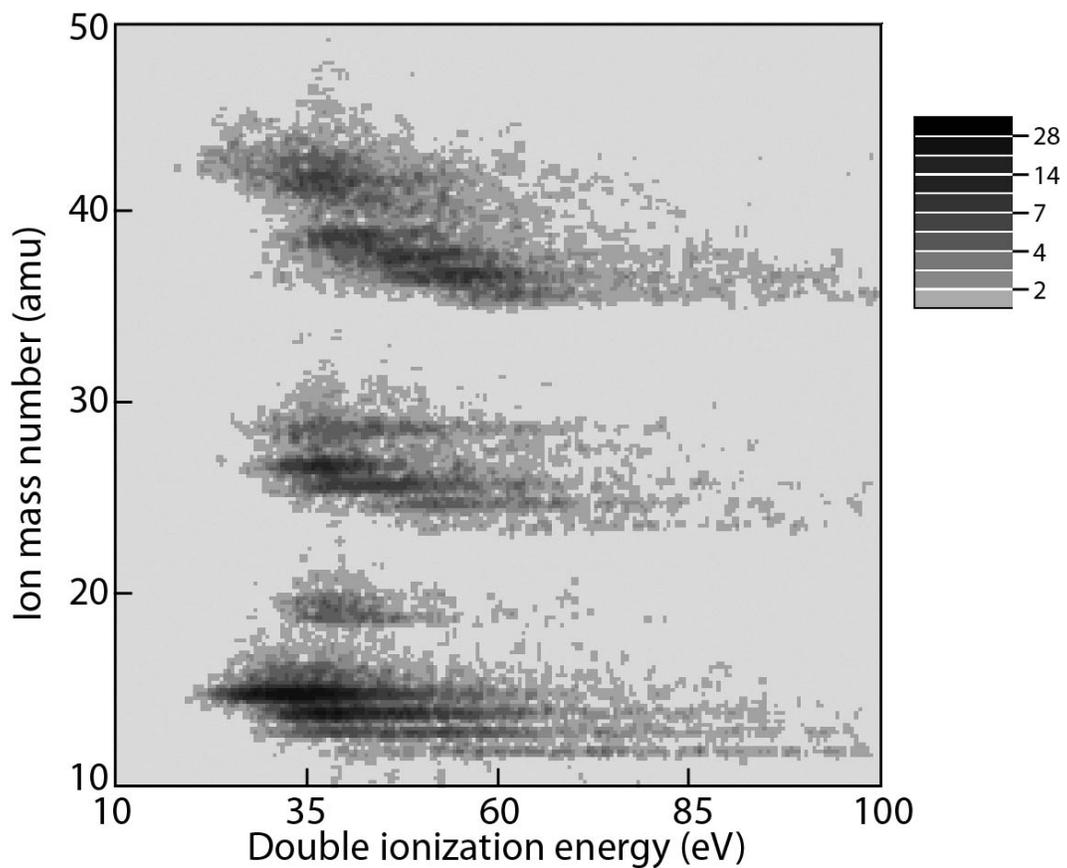


FIG. 6. Coincidence map of ion mass against binding energy of the doubly ionized acetone ions produced by Auger decay from a 1s hole on the CH_3 -carbon of acetone. The parent ion mass number would be 58. This figure is from threefold coincidences measured at 310 eV photon energy.

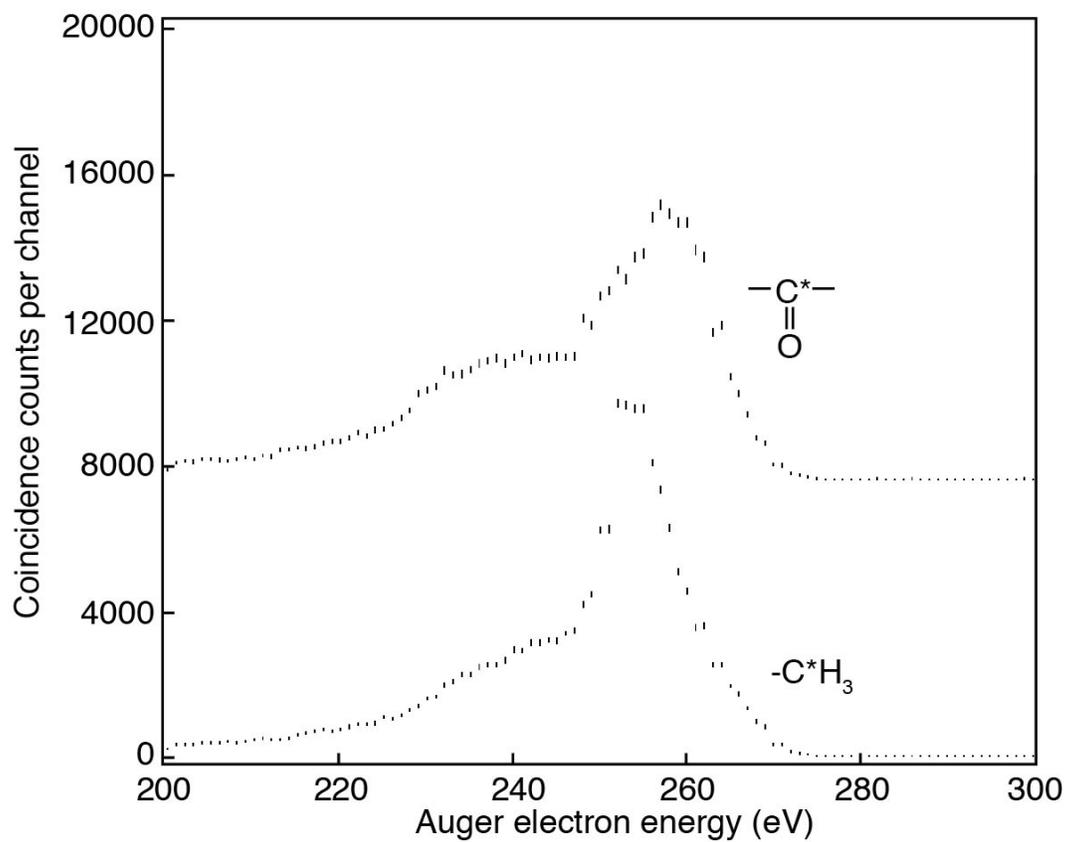


FIG. 7. Auger spectra from the distinguishable C1s sites in acetone. For this measurement the photon energy was 310 eV and no retarding potential was applied to the flight tube.

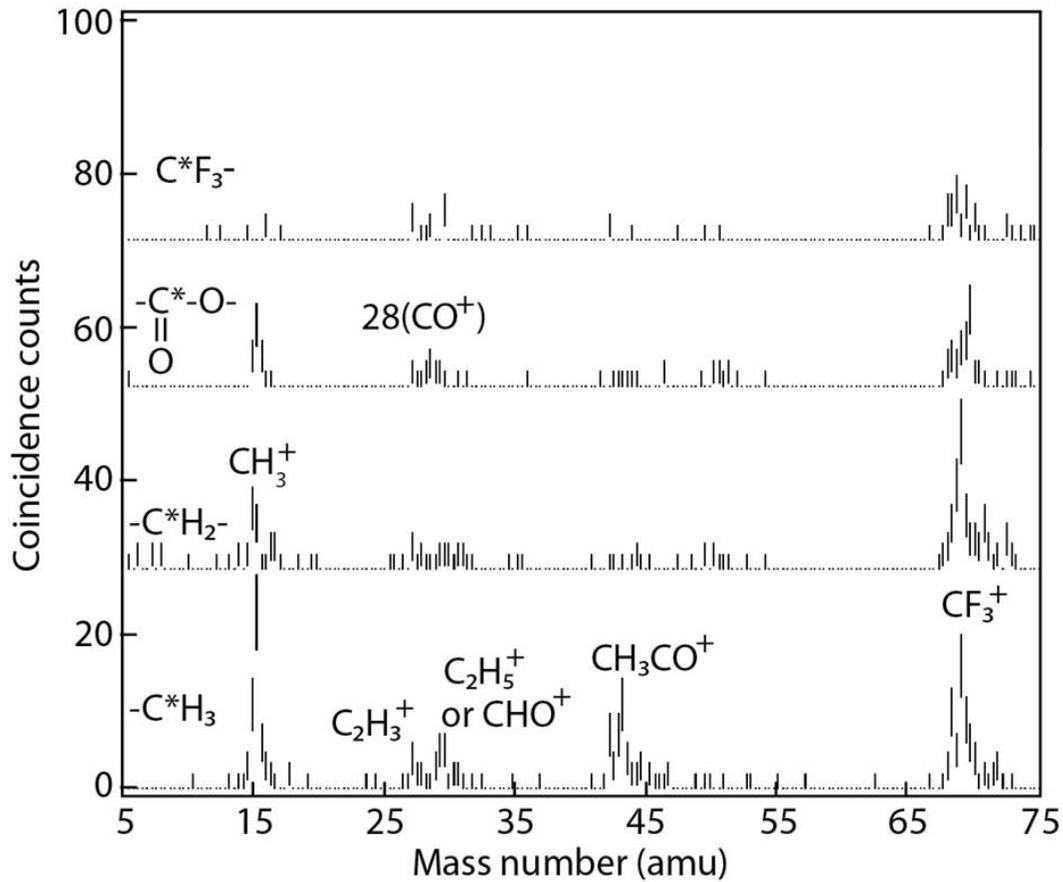


FIG. 8. Mass spectra of ethyl trifluoroacetate produced by initial C1s hole formation on each carbon atom in turn, coincident with Auger electrons producing doubly charged ions with low internal energies in the fixed range 18-23 eV double ionization energy. The measurement was made at 307 eV photon energy.