# Photoelectron Soft X-Ray Fluorescence Coincidence Spectroscopy on Free Molecules

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A technique for measuring core-level photoemission from free molecules in coincidence with the soft x-ray fluorescence decay is presented. Zero-kinetic-energy photoelectrons are detected in a time-of-flight electron spectrometer, and photons are collected in a large solid angle by a detector situated close to the interaction region. The coincidence spectrum of $N_2$ shows an adiabatic $1s$ line, free from electron-electron postcollision interaction effects. The results open up new aspects on core-hole excitation-emission dynamics.    [S0031-9007(96)00280-3]

The excitation and deexcitation of core-hole states can generally not be treated as separate processes [1]. This implies that full information about *either* of the processes can be obtained only via coincidence measurements [2]. For free molecules it has recently been shown that much can indeed be learned by measuring the Auger decay in coincidence with a photoelectron of selected energy [3,4]. In the sub-keV region, where the $1s$ binding energies of the first row elements are found, the Auger yield is typically around 99.9%, leaving 0.1% for radiative decay. Because of the low fluorescence yield there has until now been no attempt to perform coincidence spectroscopy involving the radiative decay channel at these energies [5].

With the time-of-flight (TOF) method zero-kinetic-energy (ZEKE) electrons can be extracted and detected [6,7] with very high efficiency. This technique has also been applied to threshold photoemission spectroscopy of molecular core levels [8].

In the present work we have combined a TOF electron spectrometer with a large photon detector situated close to the interaction region in order to collect radiation in a large solid angle. Using this setup we demonstrate that it is possible to measure the photoelectron spectra in coincidence with the radiative decay. The coincidence $1s$ photoelectron spectrum of $N_2$ is shown to be qualitatively different from the conventional spectrum. The difference is largely due to the elimination of the electron-electron postcollision interaction (PCI) line shape distortion. In addition we find sharp ZEKE electron soft x-ray coincidence resonances below the $1s$ ionization limit.

The experiment was carried out at the X1B undulator beam line at the NSLS in Brookhaven [9]. The monochromatized synchrotron radiation passed through a $Si_3N_4$ window into the interaction region where $N_2$ gas was let in through a hypodermic needle into the experimental chamber up to a pressure of $1 \times 10^{-4}$ torr. The soft x-ray photons and the ZEKE electrons were detected at right angles to both the propagation and polarization directions of the incoming linearly polarized photon beam, in a recently constructed instrument (Fig. 1). The electron spectrometer uses separate extraction and acceleration fields and a drift distance that results in a total TOF of 150 ns for the ZEKE electrons. These are detected in a 40 mm double multi-channel plate (MCP) detector. A similar design has been used earlier by Heimann *et al.* [7]. The photon MCP detector is situated close to the interaction region and collects radiation in about 10% of the total solid angle. A polyimide filter with a soft x-ray photon throughput of 70% is placed in front of the detector to discriminate against charged particles. The photon signal is delayed to account for the drift time of the ZEKE electrons and the coincidences are measured with time windows of 10 ns. With this simple setup a peak count rate of about 1 count/h was achieved. There are prospects of enhancing the sensitivity
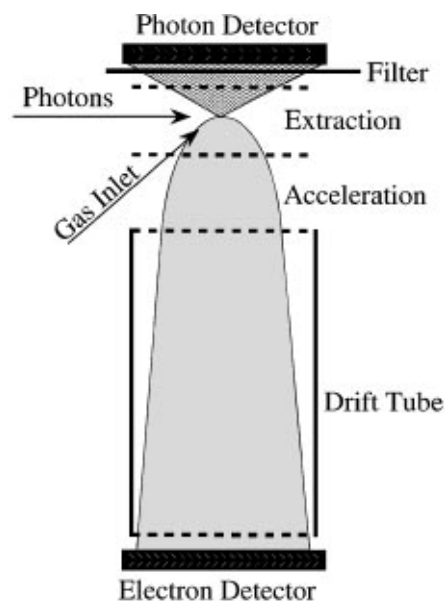


FIG. 1. Schematic experimental setup. The total electron time of flight is around 150 ns for the ZEKE electrons. The filter is polyimide, and the photon detector covers around 10% of the total solid angle.

of the method by several orders of magnitude. The sensitivity of the TOF spectrometer was limited by saturation in the MCP detector, a problem which can easily be solved using pulsed extraction fields. The sensitivity of the photon detector can also be increased by a photon-electron converting surface coating. In the future we will incorporate these improvements. In principle the experimental situation is ideal for coincidence measurements, as the ZEKE electron detection probability is very high while the total event rate is so low that accidental coincidences are rare.

The results for the 1s threshold region of the $N_2$ molecule are shown in Fig. 2. The ZEKE electron spectrum (middle curve of Fig. 2) is very similar to the one measured by Medhurst et al. [8]. All structures below the 1s ionization threshold correspond to structures in the absorption spectrum [10]. The conventional ZEKE electron spectrum shows a prominent peak with an intensity maximum at 410.3 eV, notably above the ionization limit at 409.94 eV [10]. It has a FWHM of 0.75 eV and is asymmetric with a tail at higher excitation energies. This peak is commonly interpreted as being due to the direct emission of 1s photoelectrons [8].

In the vicinity of the 1s ionization threshold the fluorescence intensity (bottom curve of Fig. 2) is almost independent of the excitation energy. No fine structure or edge behavior can be detected in the spectrum. In this respect
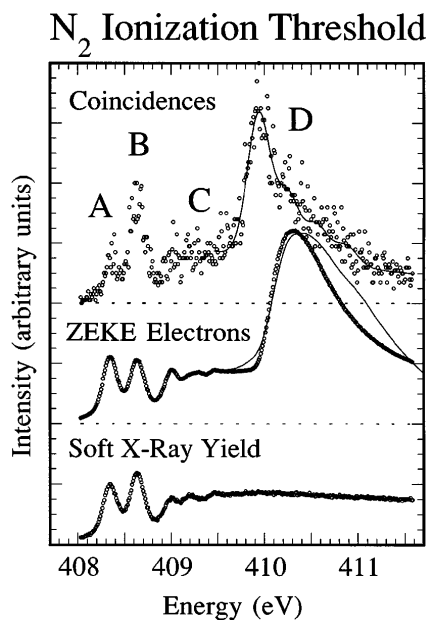
## $N_2$ Ionization Threshold



FIG. 2. From top to bottom, the coincidence spectrum, the ZEKE electron spectrum, and the soft x-ray fluorescence yield spectrum of the $N_2$ molecule. The solid line drawn through the ZEKE electron spectrum is a convolution of the coincidence spectrum and a semiclassical PCI function [15]. The solid line drawn through the coincidence spectrum is a four Gaussian fit with the energy spacing locked to 0.31 eV. The energy scale is calibrated using the absorption spectrum of Chen, Ma, and Sette [10] The three spectra are measured simultaneously, ensuring their relative calibration.

the fluorescence yield spectrum agrees with the absorption spectrum [10]. Using fluorescence yield and ZEKE electron spectroscopy *alone* it is not possible to separate the higher Rydberg excitations from continuum excitations. Also the electronic deexcitation spectra show a smooth threshold behavior at the ionization limit [11]. This indicates that the distinction between the excitation of a highly excited neutral state and a threshold ionized state is nontrivial.

The ZEKE electron spectrum measured in coincidence with the soft x-ray fluorescence (top curve of Fig. 2) is distinctly different from both the separate channels. The spectrum is dominated by a peak immediately at the core ionization threshold. This peak displays an asymmetric tail towards higher energies and possibly some fine structure as indicated by the thin solid line drawn through the data points. This line is based on a tentative fit that assumes four Gaussians of equal width and an energy spacing of 0.31 eV, as expected for vibrational excitations [8,12,13], on a linear background. The fit gives a full width at half maximum of 0.28 eV, and a peak position at 409.93 eV, which is close to the core level binding energy. The intensity ratio for the four components is 100/45/26/14, suggesting that the relative vibrational intensities are closer to what is found on shape resonance excitation [13] than to what is expected in the Franck-Condon limit [8]. Because of the limited statistics we cannot be conclusive on this point. We cannot rule out a small contribution from accidental coincidences, which would result in an apparent intensity enhancement of the higher vibrational excitations in peak *D*.

At conventional close-to-threshold photoionization the interdependence of the excitation and emission processes is manifested in the PCI between the slow photoelectron and the Auger electron. The photoelectron is retarded due to the change in ion potential associated with the decay, and the Auger electron is correspondingly accelerated. At high-flux synchrotron beam lines it has today become possible to pursue core-level photoemission spectroscopy of small molecules with a resolution that permits an analysis of the inherent line shapes [14]. At close to threshold excitation, however, the PCI distortion often obstructs a quantitative line shape analysis, and a high background of slow electrons makes it difficult to extend the measurements all the way down to the threshold. This is unfortunate since excitation-emission dynamics become particularly interesting in the immediate vicinity of the threshold.

We have used the coincidence data to simulate the conventional ZEKE spectrum applying the semiclassical theory of Niehaus [15]. The result of this transformation is given by the solid curve drawn through feature *D* in the experimental ZEKE electron spectrum (middle curve of Fig. 2). The close resemblance between this curve and the data points demonstrates that the principal difference between the conventional and the coincident ZEKE electron spectrum indeed is the elimination of the PCI effect.

Thus, we have demonstrated that using the coincidence technique it is now possible to investigate the core level photoemission process immediately at threshold. With improved statistics these data will reveal new information about the lifetime broadening, excitation cross sections, and the vibronic coupling at threshold.

In addition, the coincidence data allow for new insights regarding finer details in the core-hole excitation-emission dynamics, e.g., one can now experimentally address the question on how the x-ray decay influences a slow photoelectron, or a highly excited Rydberg electron. In the following we briefly discuss these effects by turning our attention to the region below threshold. At excitation below threshold the core state is neutral, and therefore the detected ZEKE electrons must be emitted in a secondary process.

Below theshold the ZEKE electron spectrum is very similar to the absorption spectrum [10]. This similarity extends also to the relative intensities of peak $A$ at 408.35 eV, peak $B$ at 408.63 eV as well as the fine structure in region $C$ around 409 eV. Peaks $A$ and $B$ have been assigned to the $4s\sigma$ and $4p\pi$ Rydberg states [10]. Recently the electronic decay spectrum excited at peak $B$ has revealed a contribution also from double excitations to this feature [16]. The structures in region $C$ are attributed to a series of higher Rydberg excitations converging to the ionization limit at 409.94 eV [10].

In the fluorescence yield spectrum we also observe peaks $A$ and $B$ and the fine structure in region $C$. However, in this case the relative intensities differ markedly, in particular the relative strength of peaks $A$ and $B$ is reversed, and the intensities in region $C$ are redistributed. We tentatively ascribe the differences between the intensities of the fluorescence yield and the absorption spectra below threshold to an anisotropy effect due to the polarization of the incoming radiation [17].

In comparison with these independently collected data curves the coincidence spectrum exhibits some obvious differences. The intensity ratio comparing peaks $B$ and $A$ is much larger in the coincidence spectrum than in the separate channels. Additionally, the "unstructured signal" in the coincidence spectrum decreases, comparing the intensity at 409.5 and 411.5 eV. This is also expressed by the fact that the background of the curve fit of the coincidence spectrum shown in the top curve of Fig. 2 is slanted. Thus, the coincidence intensity below threshold is higher than above threshold. Effectively, there is a stepdown at threshold in the coincidence ZEKE electron intensity that is absent in both the separate channels.

In a simple "multiple-step" picture for the intensity below threshold, the $1s$ electron is excited to a Rydberg orbital in the initial step. The ZEKE electron can then be emitted either as a shakeoff electron during the second radiative decay step, or via a third step: the Auger decay of the valence-hole Rydberg state which is populated in a (second step) radiative decay where the excited Rydberg electron is spectator. Both these processes may contribute

to the intensity below the core ionization threshold. For an understanding of the finer details in the spectrum, theoretical developments are necessary.

In conclusion, we have demonstrated the feasibility to measure threshold core-level photoelectron spectra of free molecules in coincidence with the radiative decay in the sub-keV region. The results include the adiabatic $1s$ photoemission line of $N_2$, free from electron-electron PCI, as well as structure below the ionization limit. The coincidence spectrum is dramatically different from the conventional spectrum, and it demonstrates that it is essential to eliminate the electron-electron PCI to observe the finer details of the core-hole excitation-emission dynamcis at the ionization threshold.

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vector of the radiation, whereas $\pi$ orbital excitation is possible only when the molecular axis is perpendicular to the polarization. The probability for detection of emission from $\pi$ orbitals is relatively enhanced when the molecular axis is perpendicularly oriented to the photon detector surface. In our experimental geometry this orientation is realized only by excitation to Rydberg $\pi$ orbitals. In general we expect more fluorescence intensity from the valence $\pi$ than from the $\sigma$ orbitals [12], and hence a higher fluorescence yield by excitation to $\pi$ orbitals. This confirms the assignment of peaks A and B as $\sigma$ and $\pi$ resonances, respectively, and also the assignment of the first sharp feature in structure C as a $\sigma$ type Rydberg excitation. We cannot rule out, however, that other effects influence the florescence yield (FY) intensities. The selection rules associated with the inversion symmetry may influence the FY slightly different for the various Rydberg states. For a definite conclusion information on the angular dependence is required.