Molecular-frame angular distribution of normal and resonant Auger electrons

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Abstract. Molecular-frame angular distributions (MFADs) of resonant and non-resonant (“normal”) Auger electrons were determined using angle-resolved electron-ion coincidence spectroscopy. Here, we concentrate on the MFADs of normal N\textsubscript{2} KVV Auger electrons. We conclude that their MFADs are independent of both photon energy and light polarization direction, thus confirming that the two-step model is a good approximation. All threshold and shape-resonance phenomena can be attributed to the absorption process and are irrelevant for the Auger decay in the molecular frame. Distinct differences in the MFADs are found as a function of the Auger final state.

1. Introduction

Molecular-frame angular distributions (MFADs) of photo- and Auger electrons offer an unprecedented level of detailed information on the photoionization dynamics of (small) molecules, which are hidden in conventional gas-phase electron spectroscopy due to the random orientation of the molecules that averages out most characteristic intensity modulation. In order to experimentally determine MFADs, the molecules have to be “fixed” in space. For dissociative photoionization, this can be realized by applying the angle-resolved photoelectron-photoion coincidence technique \cite{1, 2, 3}, which has developed rapidly with the advent of position-sensitive detectors \cite{4, 5, 6, 7}. While most of these studies to date have focused on photoelectrons \cite{8, 9, 10, 11, 12, 13, 14, 15, 16, 17}, only few studies on Auger electrons have been performed. Apart from a measurement of the MFAD of Auger electrons in N\textsubscript{2} after electron impact \cite{18}, only two studies of Auger electron MFADs after photoexcitation of CO \cite{19, 20} have been reported prior to our recent series of measurements. Since our recent results for resonant and non-resonant Auger decay in CO have already been described in detail \cite{21, 22, 23}, the present paper focusses on our results obtained for non-resonant Auger electrons in N\textsubscript{2}.

2. Experimental Method

In contrast to most experiments that determine the photoelectron molecular-frame angular distributions, we did not record the emitted Auger electrons in a wide range of angles, but rather...
fixed the direction of the Auger electron detection while measuring the full three-dimensional ion angular distribution for two different orientations of the polarization vector. Assuming the validity of a strict two-step model, i.e. assuming that the Auger electron emission characteristics are independent of the initial ionization step, the coincident ion distribution should be a product of the angular selectivity of the ionization process and the molecular-frame angular distribution of the Auger electrons. The probability $I_{ei}(\vec{e}, \vec{n}, h\nu)$ to find an electron in the directions $\vec{e}$ in coincidence with an ion in the directions $\vec{n}$ at a given photon energy $h\nu$ is simply the probability $I(\theta^E_n, h\nu)$ to ionize a molecule with the axis aligned in the direction $\vec{n}$ at an angle $\theta^E_n$ to the polarization vector multiplied by the probability that this molecule emits an electron towards the electron detector, which is given by the molecular-frame angular distribution of Auger electrons, MFAD($\theta$). The angular selectivity, $I(\theta^E_n, h\nu)$, of the initial ionization process is described by the photon energy dependent molecular alignment parameter, $\beta_m$, and $I_{ei}(\vec{e}, \vec{n}, h\nu)$ can thus be expressed as

$$I_{ei}(\vec{e}, \vec{n}, h\nu) \propto (1 + \beta_{mol}(h\nu) \cdot \frac{3 \cdot \cos^2(\theta^E_n) - 1}{2}) \cdot MFAD(\theta).$$ (1)

Therefore, if $\beta_m$ is known and the two-step model is assumed, a measurement of the angular distribution of ions coincident with Auger electrons emitted in a fixed direction is sufficient to determine MFAD($\theta$). At the same time, the validity of the strict two-step model can be tested within the same experiment by repeating the measurement with two different polarization directions of the light and with different photon energies, thus checking the consistency of the two corresponding molecular-frame angular distributions. Note that this method is slightly different from the one used in our work on the MFADs of resonant CO Auger electrons [21, 22], which was performed at the Advanced Light Source using a modified velocity map (VMI) ion imaging spectrometer [24] in combination with two electron time-of-flight analyzers [25] and which thus allowed measuring the MFADs without making further assumptions regarding the two-step model.

The present experiment was performed at the high-resolution photochemistry beamline 27SU at SPring-8 using the identical setup as for our measurement of the non-resonant Auger electron MFADs in CO [23]. CO was introduced as an effusive beam crossed by the synchrotron radiation. The pressure in the vacuum chamber was $2.0 \times 10^{-4}$ pa. The Auger electrons were measured in a hemispherical electron analyzer, for which a pass energy of 200 eV and an instrumental resolution of about 1 eV were used. The photon energy bandwidth was 120 meV. A pulsed-field velocity focussing ion time-of-flight (TOF) spectrometer [26] was mounted opposite to the electron spectrometer. From the exact time of flight of ions with the same mass together with the detector hit position, we reconstructed the initial ion momentum and thus the ion angular distribution.

For the coincidence experiment, all voltages of the electron spectrometer were set such only electrons in an energy interval from 354 to 371 eV were recorded. The ionizing soft x-rays were linearly polarized either horizontally along the axes of the electron spectrometer and the ion spectrometer or in the vertical direction perpendicular two both spectrometer axes. For each photon energy and each polarization direction, data was collected for about 10h. All figures shown in this paper show the data after the subtraction of the random coincidences as described in [27].

3. Results and Discussion

The N$_2$ normal Auger electrons were measured with high resolution at two photon energies, 420 eV (on the so-called “shape resonance”) and far above threshold at 500 eV. By detecting the ions produced in coincidence with the Auger electrons, we were able to disentangle the channels that
yield \( \text{N}_2^{+ +} \), \( \text{N}^+ \), and \( \text{N}^{++} \) fragments (see Fig. 1). The decay channels producing \( \text{N}^+ \) belong to four groups in the Auger spectrum labeled A through D, for which we determined the fragment ion angular distributions. For the ion angular distributions shown in Fig. 2, we analyzed \( \text{N}^+ \) ions within the kinetic energy range from 2 to 7 eV. According to electron-optical simulations, the ion spectrometer should have a 4\( \pi \) collection efficiency for \( \text{N}^+ \) ions up to 7 eV, while faster ions may miss the detector for certain emission angles. The non-uniform efficiency of the ion detector was calibrated by making use of the symmetry of the ion distributions, which have to be cylindrically symmetric around the electron emission direction and the polarization vector when both directions coincide.

In order to discuss the observed ion angular distributions, let us first turn to the measurements at 500 eV. While the angular distributions corresponding to each of the four Auger groups are noticeably different, they are (almost) identical for both polarization directions, as is expected for a photon energy far above threshold. Therefore, according to Eq. 1, the ion angular distribution in the laboratory frame is equivalent to the Auger electron angular distribution in the molecular frame.

If the two-step model underlying Eq. 1 is valid for all photon energies, the effect of the shape resonance on the measurements at 420 eV can be described by multiplying the angular distributions measured at 500 eV by a factor describing the selectivity of the molecular axis orientation in the core ionization process. Indeed, we find that this is possible for \( \beta_m = 0.75 \) at 420 eV and \( \beta_m = -0.05 \) at 500 eV. Therefore, in agreement with our findings for the normal Auger decay of CO [23], we can conclude that the two-step model is a very good approximation for the normal Auger decay of \( \text{N}_2 \). The first step, in which a core electron is emitted from the molecule, can have a high degree of selectivity for the molecular axis, especially in the shape-resonance region, which is described by the photon-energy dependent alignment parameter \( \beta_m \). However, \( \beta_m \) does not depend on the Auger final state and the Auger decay can be considered as an independent second step since the core hole state does not contain any information on the direction of the electric vector or the photoelectron emission direction. The angular distribution of the Auger electrons thus depends only on the angle with respect to the molecular axis. In other words, the Auger electron MFADs do not depend on the photon energy or on the direction of the electric vector. Therefore, a measurement of the angular distributions of ions detected in coincidence with Auger electrons emitted in a fixed direction together with the known value of \( \beta_m \) is enough to determine the MFADs. In turn, knowing the photon energy dependence of \( \beta_m \), one can predict the angular distribution of the coincident ions for any polarization direction of
**Figure 2.** Angular distribution of N\textsuperscript{+} ions in the plane containing the electric vector and the electron emission direction, measured in coincidence with an Auger electron detected along the direction marked by the horizontal white stick. The distributions for each of the four Auger groups A, B, C, and D are shown for two orientations of the electric vector, horizontal and vertical, and for two photon energies.

the light even in the photon energy region corresponding to the shape resonance.

Fig. 3 shows the molecular-frame angular distribution of N\textsubscript{2} normal Auger electrons as determined from the coincident ion angular distributions in Fig. 2. They differ distinctly for the four groups A, B, C, and D as defined in Fig. 1. For group A and B, the emission is directed primarily along the molecular axis, while it is more isotropic for group C and D. Although it is difficult to compare directly to the measurements of the Auger electron molecular-frame angular distribution by Schöffler et al [14], who did not resolve the Auger final state, we note a qualitative agreement to their angular distribution, which are dominated by the contribution from the most intense group D. The narrower and more pronounced maxima of the angular distribution measured by Schöffler et al could be attributed to a smaller effective acceptance angle for the orientation of the molecular axis in their experiment.
Figure 3. Molecular-frame angular distribution of N\textsubscript{2} normal Auger electrons in the four groups A, B, C, and D shown as polar plots in the plane containing the molecular axis (top row) and as cartesian plots as a function of electron emission angle with respect to the molecular axis (bottom row).

4. Conclusion
We have measured the angular distribution of N\textsuperscript{+} fragments in coincidence with N\textsubscript{2} Auger electrons from different Auger groups and found significant differences for the different Auger groups. Our measurements at two photon energies and for two orientations of the polarization vector confirm the validity of the two-step model for normal N\textsubscript{2} Auger decay and thus allow extracting the molecular-frame Auger electron angular distributions, which are also significantly different for the different Auger final states.

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