HIGH-RESOLUTION RESONANT AUGER ELECTRON SPECTROSCOPY FOR INVESTIGATING NUCLEAR MOTION IN CORE-EXCITED MOLECULES

Synchrotron radiation sources and the soft X-ray monochromators have been improved significantly in the past few decades. Currently, it is possible to promote a specific inner-shell electron to any unoccupied atomic and molecular orbital with an excitation photon band pass smaller than the natural width of the inner-shell excited states. In this context, the experimental width of the Auger lines is not determined by the natural width of the inner-shell excited states, but, in general, by the convolution of the excitation photon band pass and the band pass of the electron energy analysis. This line narrowing effect, often called the Auger resonant Raman effect, has been used for spectroscopic investigations of the Auger final states of rare gas atoms, as well as for investigations of the nuclear motion dynamics of the inner-shell excited molecules. The inner-shell excited molecule thus created decays mostly via the resonant Auger emission, initiating molecular dissociation. Nuclear motion, however, occurs in the core-excited state on a timescale of tens of fs, which is the lifetime of the inner-shell excited state, affecting the dissociation after the Auger decay. The objective of this study is to establish resonant Auger spectroscopy as a direct probe of the nuclear motion in the core-excited states.

Experiments were performed at the soft X-ray photochemistry experimental station (C-station) installed at beamline **BL27SU** [1]. This experimental station is designed for the study of photoionization and electronic relaxation dynamics

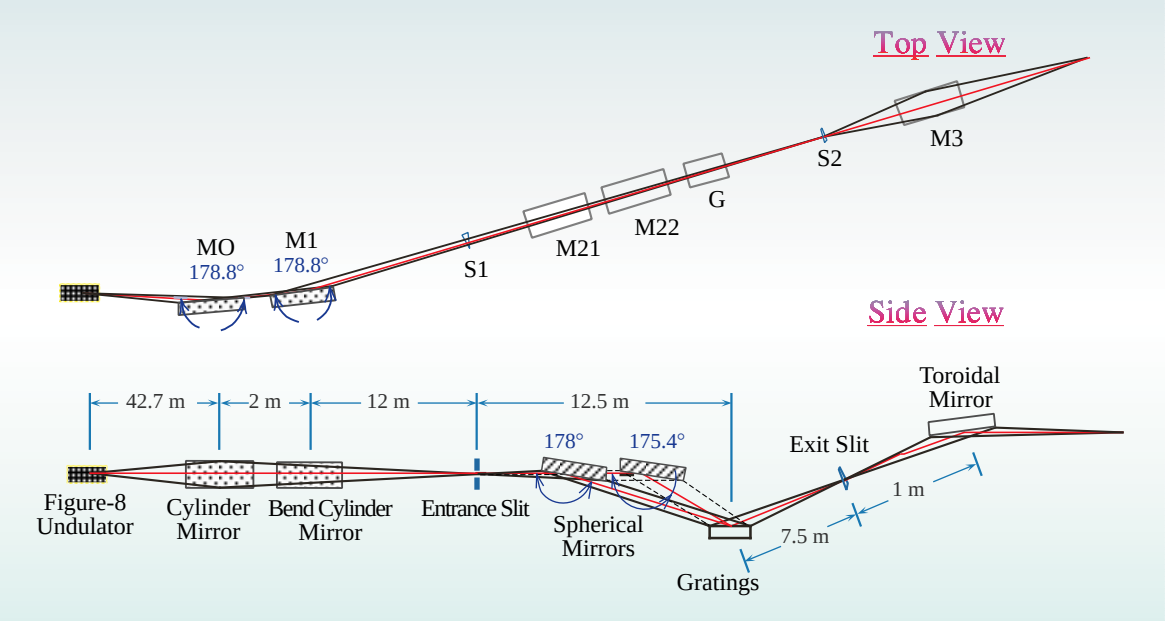

Fig. 1. Optical layout of the monochromator at BL27SU.

of core-excited atoms and molecules, as well as the observation of ion fragmentation processes of molecules by using a high resolution monochromator (E/ΔE >10000). The monochromator is of the Hettrick type, and is equipped with varied line spacing plane gratings and spherical focusing mirrors [2]. Figure 1 shows the optical layout of the monochromator. Three gratings and two spherical mirrors cover the photon energy range from 0.2 to 3 keV. By measuring the photoabsorption spectrum of rare gas atoms and N_2 in the *K*-shell excitation region, the resolving power (E/ΔE) is estimated tentatively. For example, Fig. 2 shows the Ne photoabsorption spectrum in the $1s \rightarrow np$ Rydberg resonance excitation region. The $1s \rightarrow np$ (n= 3 - 6) transitions are clearly discerned in the spectrum. Comparison with other high-resolution photoabsorption measurements leads an estimated resolving power (E/ΔE) of better than 10000. The details of the monochromator and the performance tests have been reported in recent articles [3-5].

In the past year, we have installed a high-resolution electron energy spectroscopy apparatus (GAMMADATA-SCIENTA SES 2002 with a tunable gas cell GC-50) onto the beamline as a part of the end station and initiated the subnatural-width resonant Auger electron spectroscopy of atoms and molecules [6-8]. The first result of this investigation using the Ne $1s \rightarrow 3p$ excitation is as follows. Figure 3 shows the observed resonant Auger emission lines, whose final states are $Ne^+2p^{-2}(^1D_2)3p$. The photon band pass and the band pass for the electron energy analyzer are 60-68 meV and 13 meV, respectively, while the Doppler width due to thermal motion of the Ne atoms is 79 meV. The measured width of 100 - 105 meV is the convolution of these three widths and is much smaller than the natural width of the Ne 1*s* hole state (~ 250 meV). At this resolution, we distinguished for the first time three multiplet components — ^2P, ^2D, and ^2F — and confirmed that the measured values of the anisotropy parameter β for these three are in excellent agreement with the theoretical predictions [8].

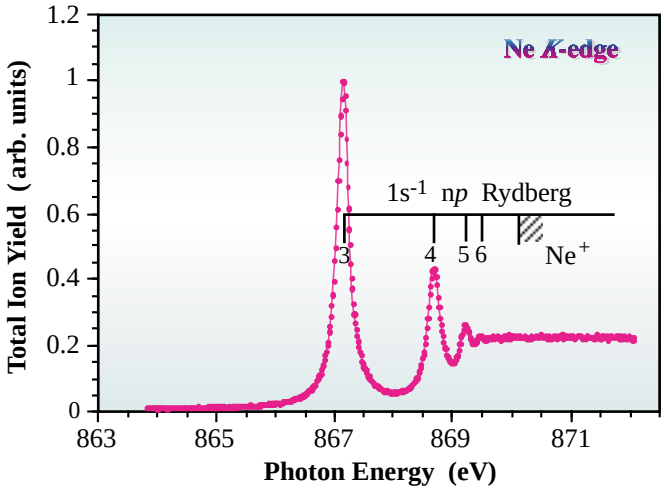

Fig. 2. Total ion yield spectrum of Ne at K-edge.

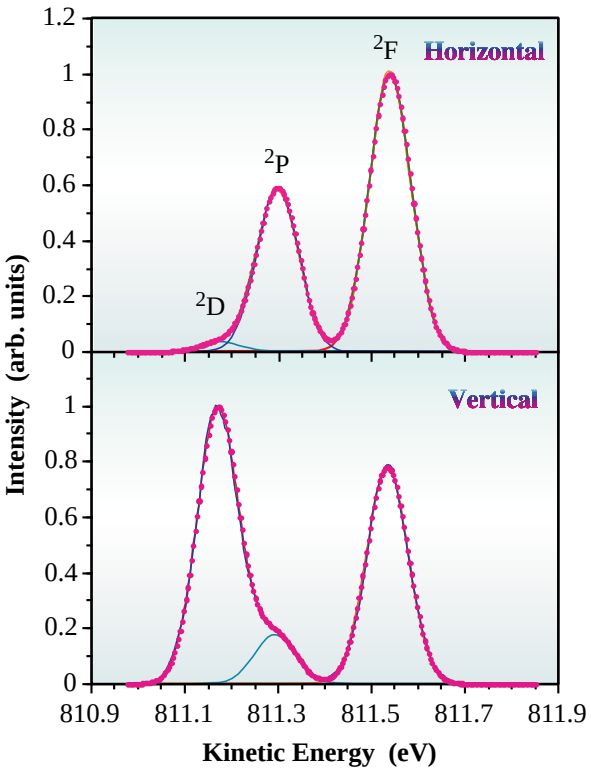

Fig. 3. Part of the electron spectra of the resonant Auger transitions from the Ne $1s^{-1}3p$ state to the final Ne^+ $2p^{-2}$ ($^1D_2$)3p — ^2D, ^2P and ^2F — states recorded at a photon energy of 867.12 eV with horizontal (upper) and vertical (lower) polarizations. The electron spectrometer axis is in the horizontal direction.

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