

Subnatural Linewidths in Core Level Excitation Spectra

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We have measured a core excitation spectrum on the N_2 $1s \rightarrow \pi^*$ transition in which the experimental linewidth is limited by the instrumental resolution rather than by the lifetime of the core hole. The measurement is performed by recording the partial yield of resonant Auger electrons within a fixed kinetic energy window. The factors contributing to the line shape and the general applicability of the method are discussed. [S0031-9007(98)06577-6]

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Recent developments in undulator and soft x-ray monochromator technology have led to an upsurge in high-resolution studies of electronic transitions involving the inner shells of atoms and molecules [1–3]. In these cases the measured linewidths are barely perturbed by the interaction of the atom with its surroundings. The important inherent broadening factor is the lifetime of the core-hole state. There are, however, possibilities of overcoming inherent lifetime widths. Whereas Auger decay linewidths for core-ionized states have always been found to be larger than the lifetime width, this is not the case for neutral core-excited states. In fact, in the last few years many resonant Auger spectra of atoms and molecules have even been recorded with subnatural linewidths [4–6]. In such experiments, which require narrow photon band excitation, the energy of decay lines is expected to follow linearly the photon energy. The observed line narrowing and linear energy dispersion are expected from resonant Raman scattering theory that treats excitation and deexcitation as a single scattering event [7]. A line sharpening effect in photon energy dependent scans was also observed in electron yield spectra from the solid state by Drube *et al.* [8]. These authors compared the total electron yield around L_3 -to-conduction band resonances in several metals to the partial yield obtained by setting an energy window on an L_3 Auger decay. The latter spectra showed more fine structure above the Fermi edge. An apparent resolution enhancement by an analogous method in resonant x-ray scattering was seen by Hämäläinen *et al.* [9].

In the present paper we report partial electron yield spectra for the N_2 molecule in which a conceptually different approach has been used. The measurement has been performed at the well-separated core-to-bound state transition $1\sigma_u \rightarrow 1\pi_g$, also denoted as the π^* resonance, rather than across several different electronic states or even above the ionization threshold. Furthermore, we exploit the unusual but quantifiable characteristics of the resonant Auger decay to the $1\pi_u^{-1}$ single-hole final state. This so-called participator transition does not show an appreciable energy dispersion in decay spectra taken at

the maxima of the different vibrational components of the $1\sigma_u^{-1}1\pi_g$ core-excited state. A definite sharpening of the absorption features is observed making them narrower than the core-hole lifetime width.

The partial electron yield and resonant Auger spectra of N_2 were measured on the X1B undulator beam line [10] at the National Synchrotron Light Source (NSLS), Brookhaven, using a “magic angle” cylindrical mirror analyzer (CMA) [11]. The photon energy resolution of the spherical grating monochromator was 50–60 meV with the entrance and exit slit set at 5 μm . For the studied transition at $E_{\text{kin}} \approx 384$ eV the energy resolution of the electron analyzer was between ~ 164 and ~ 221 meV, depending on the pass energy. The N_2 $1\sigma_u \rightarrow 1\pi_g$ excitation spectrum has been the subject of numerous investigations, partly because it has become a benchmark test for the photon energy resolution of grazing incidence monochromators. Astonishingly, the lifetime broadening of the core-excited state is not accurately known. A total absorption linewidth of 118 meV for the transition $1\sigma_u \rightarrow 1\pi_g$, $\nu' = 0$ has recently been achieved at the synchrotron radiation source Elettra, Trieste [12]. From this a Lorentzian lifetime width of $113(\pm 3)$ meV was estimated using the expected Gaussian monochromator function of 25 ± 5 meV and the numerical results of Lee [13].

Figure 1 shows a core-excitation spectrum measured in the partial electron yield mode using low kinetic energy secondary electrons ($E_{\text{kin}} \sim 1$ eV). This kind of yield measurement can be considered to reproduce correctly the shapes and energies of features in the corresponding absorption spectrum, but not necessarily their relative intensities. At the ionization threshold yield spectra measured with secondary electrons also tend to rise more steeply than in true photoabsorption. The spectrum of Fig. 1, nevertheless, resembles previously published photoabsorption spectra. The decomposition shown is from a larger set in which four spectra taken with different slit widths were fitted simultaneously so that the lifetime broadening and vibrational energies were constrained to have identical values. For an absorption-type measurement the experimental line shape is the

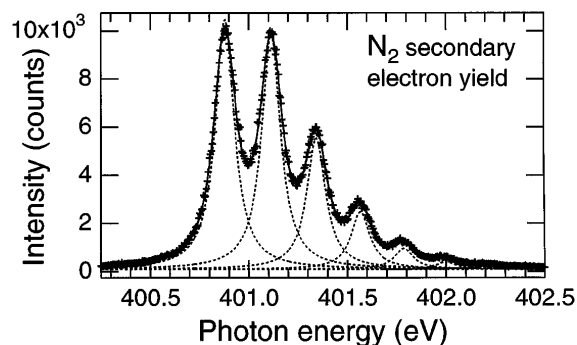


FIG. 1. Partial electron yield spectrum of secondary electrons at the N_2 $1s \rightarrow \pi^*$ excitation. The analyzer monitored ~ 1 eV electrons with a 300 eV pass energy. The monochromator resolution was about 54 meV (slits $5/5 \mu\text{m}$). This curve has the form of the normal photoabsorption spectrum.

convolution of the Lorentzian lifetime broadening and the monochromator bandpass function. The latter was represented here by a Gaussian. The fit yielded a lifetime width of 116 meV and a photon energy resolution of 49 meV for the slit settings $5/5 \mu\text{m}$ that were used for the spectrum of Fig. 1. The total line width is about 135 meV. The vibrational energy ω_e and the anharmonicity $\omega_e x_e$ of the $1\sigma_u^{-1}1\pi_g$ state were found to be 241 ± 1 meV and 2.9 ± 0.5 meV, respectively. As the extracted lifetime broadening is slightly larger than in the Elettra result, which has to be considered more reliable, the monochromator bandpass function at the X1B beam line is probably not exactly Gaussian. Monochromator line widths used in the rest of this work have been increased by 5 meV to bring them in line with the smaller value for the lifetime.

The line shape in resonant Auger electron spectra excited with finite photon bandwidths has been considered in detail by Kukk *et al.* [14]. Consider the energy distribution of a core-excited state to have a Lorentzian line shape L which peaks at an energy ϵ_0 . When this state is excited from the ground state using a photon band designated by M and centered at an energy ϵ_c , the intensity distribution $I(\epsilon)$ of the core-excited state is given by

$$I(\epsilon) \propto M(\epsilon - \epsilon_c)L(\epsilon - \epsilon_0). \quad (1)$$

This product is sharper than either of the contributing distributions, i.e., it is narrower than the lifetime profile of the corresponding core-excited state. In electron spectroscopy of a resonant Auger line, the photon energy and bandwidth are held constant, while the voltages of an electron spectrometer are swept in order to detect electrons of different kinetic energies. The observed line shape of the resonant Auger line is the convolution of the line shape $I(\epsilon)$ with the bandpass function A of an analyzer set to detect electrons having a kinetic energy $\epsilon_A = \epsilon_0 - \epsilon_f$, where ϵ_f is the binding energy of the final state. We get

$$P_{\text{RA}}(\epsilon_A) = \int_0^\infty I(\epsilon)A[\epsilon_A - (\epsilon - \epsilon_f)]d\epsilon. \quad (2)$$

The decay of the $1\sigma_u^{-1}1\pi_g$ core-excited state of N_2 takes place mainly via electron emission. The interpretation of the resonant Auger spectrum in terms of participator and spectator transitions, which give rise to $1h$ and $2h-1p$ final states, respectively, was first given by Eberhardt *et al.* [15]. The most intense participator transition, to the $1\pi_u^{-1}$ final state, has a regular vibrational fine structure that can be interpreted on the basis of transitions during which the vibrational quantum number does not change. This has been attributed to the similarity of the potential energy curves in the core-excited and final states. Figure 2 shows the $1\pi_u^{-1}$ participator peak measured at the maximum of the $1\sigma_u \rightarrow 1\pi_g$, $\nu' = 0$ excitation. The spectrum is dominated by the transition to the $\nu' = 0$ final state. A small shoulder, however, appears on the low kinetic energy side. It arises from the $1\sigma_u^{-1}1\pi_g$, $\nu' = 1 \rightarrow 1\pi_u^{-1}$, $\nu' = 1$ transition, which is excited at the tail of the Lorentzian lifetime profile (see Fig. 1). The spectrum has been fitted according to Eqs. (1) and (2). The product $M(\epsilon - \epsilon_c)L(\epsilon - \epsilon_0)$ was calculated by multiplication of a 54 meV Gaussian for the monochromator and a 113 meV Lorentzian. The resulting profile having a 48 meV FWHM value was convoluted with an asymmetric Gaussian (for the CMA) in order to reproduce the experimental spectrum. The kinetic energy resolution thus extracted was 164 meV (7.5 eV pass energy).

When the photon energy was scanned across the resonance, the vibrational components of the participator peak showed, as expected, energy dispersion. However, at the photon energies corresponding to the vibrational maxima of the core-excited state, the participator transition for which there was no change in the vibrational quantum number always occurs at essentially the same kinetic energy. This can be checked more rigorously using the spectroscopic constants ω_e and $\omega_e x_e$ of the states involved; those of the $1\pi_u^{-1}$ final state are $\omega_e = 236.0$ meV and $\omega_e x_e = 1.86$ meV [16]. Accordingly, the kinetic energy of the participator transition $1\sigma_u^{-1}1\pi_g \rightarrow 1\pi_u^{-1}$,

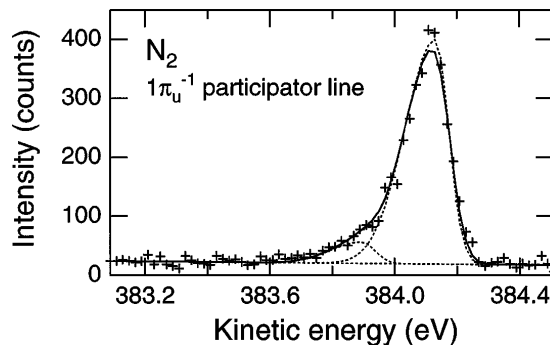


FIG. 2. The $1\pi_u^{-1}$ participator peak measured at the maximum of the $1\sigma_u \rightarrow 1\pi_g$, $\nu' = 0$ excitation. Analyzer pass energy = 7.5 eV; photon energy resolution ~ 54 meV. The dashed lines depict the shape of the analyzer transmission profile.

$\Delta\nu' = 0$ should occur within a 15 meV range for vibrational quantum numbers $\nu' = 0-5$.

The constant kinetic energy of the $1\pi_u^{-1}$ participator peak motivated us to use it for a partial electron yield measurement at the π^* resonance. Two somewhat surprising spectra, obtained with 7.5 and 15 eV pass energies for the CMA, are shown in Fig. 3. In comparison to the spectrum of Fig. 1, these partial electron yield spectra appear to be much better resolved. This is also supported by the FWHM value of the peaks which are about 113 and 127 meV for Figs. 3(a) and 3(b), respectively. Yet the photon energy resolution was similar in the two types of measurements; the spectra of Figs. 1 and 3 were taken consecutively with the same slit widths. The line shapes are also different. In contrast to the partial yield of secondary electrons (Fig. 1), the partial electron yield of the resonant Auger electrons (Fig. 3) is composed of narrow-based peaks that do not resemble Lorentzians at all, i.e., the lifetime contribution appears to be suppressed. The vibrational spacings in the spectra of Figs. 1 and 3 are identical within the accuracy of the fit.

How can the appearance of the spectra in Fig. 3 be explained? Let us consider what happens in the measurement. Starting with a photon energy set on the low-energy tail of the first resonance, the core-excited state is created with the probability distribution given

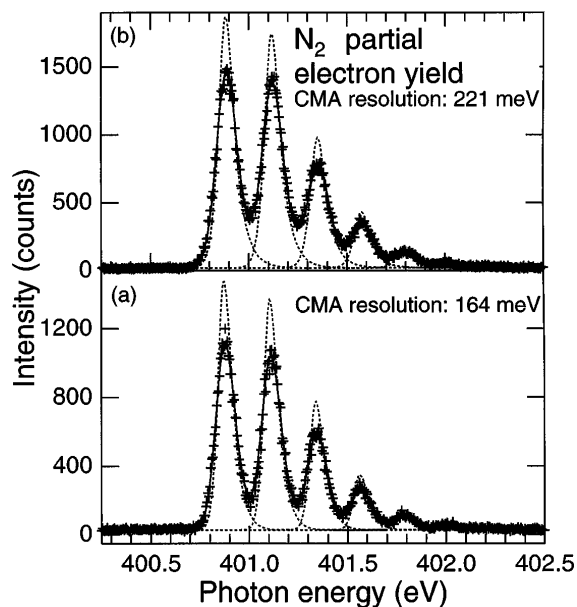


FIG. 3. Partial electron yield spectrum at the N_2 $1\sigma_u \rightarrow 1\pi_g$ excitation using 384.2 eV electrons. This kinetic energy corresponds to that of the participator transition $1\sigma_u^{-1}1\pi_g \rightarrow 1\pi_u^{-1}$, $\Delta\nu' = 0$. The pass energies of the analyzer were (a) 7.5 eV and (b) 15 eV, equivalent to the kinetic energy resolutions of ~ 164 and ~ 221 meV, respectively. Note the apparently higher resolution of the spectra as compared to Fig. 1 obtained at identical monochromator settings. The dashed curves show the line profiles before the convolution with the monochromator function.

by Eq. (1). The core-excited state, of course, decays. Because of the energy dispersion, however, the kinetic energy of the $1\sigma_u^{-1}1\pi_g \rightarrow 1\pi_u^{-1}$ participator transition is too low to fit in the relatively narrow bandpass profile of the analyzer. The partial electron yield spectrum therefore shows no intensity at this photon energy, in contrast to a normal absorption measurement. The analyzer removes all electrons that do not have the correct kinetic energies. Indeed, if the analyzer window is narrow, the photon energy needs to be very close to the first vibrational maximum of the core-excitation spectrum for resonant Auger electrons to be detected. This gives a steep flank in the spectrum, since at the same time the core-excitation probability is also reaching the (first) maximum. On the high-energy side of the $1\sigma_u \rightarrow 1\pi_g$, $\nu' = 0$ excitation, the kinetic energy of the participator line becomes too large to give any partial yield intensity. The first peak in the yield spectrum therefore acquires a steep high-energy flank. Because of the nearly identical kinetic energies for the participator transitions $1\sigma_u^{-1}1\pi_g \rightarrow 1\pi_u^{-1}$, $\Delta\nu' = 0$, similar considerations are valid also for the decay from the higher vibrationally excited intermediate states.

The line shape of this kind of partial yield measurement can be constructed heuristically from the analogy with the resonant Auger measurement. The function of the bandpass filter is now performed by the electron analyzer rather than by the monochromator. This suggests that the Lorentzian lifetime profile L should be multiplied by the analyzer bandpass function A in order to get the intensity distribution at an excitation energy ϵ :

$$I(\epsilon) \propto L(\epsilon - \epsilon_0)A[(\epsilon_0 - \epsilon_f) - (\epsilon - \epsilon_f)]. \quad (3)$$

The scanning of the photon energy during the partial electron measurement in turn implies the convolution of the above product by the monochromator bandwidth $M(\epsilon)$. Thus we arrive at the line shape formula for an isolated partial electron yield peak:

$$P_{PY}(\epsilon_c) = \int_0^\infty I(\epsilon)M(\epsilon - \epsilon_c) d\epsilon. \quad (4)$$

If the partial decay probability to a given final state is not exactly proportional to the absorption cross section, Eq. (3) should be multiplied by the corresponding probability function, say $D(\epsilon - \epsilon_0)$. Recent measurements on the decay branching ratios to the different final states at the $C 1s \rightarrow \pi^*$ resonance in CO [6] demonstrated the necessity of including the function D .

The fits shown in Fig. 3 have been performed using the line shape equation (4) on a set of seven spectra taken with different combinations of pass energies and slit settings. There is good agreement with the experimental data. Note especially the tail on the high-energy flank of the partial yield peaks, which is due to the asymmetry of our CMA transmission profile. Nevertheless, values for the monochromator widths resulting from this fit are 10–20 meV larger than from the low kinetic energy

yield (Fig. 1). This may result from other approximately Gaussian apparatus effects, e.g., instability of the spectrometer voltages. In Eq. (3) the line width in the partial electron yield measurement of resonant Auger electrons depends directly on the kinetic energy resolution, as is verified by the measurements of Fig. 3. The bandpass profile of the analyzer does not have to be smaller than the lifetime width of the core hole in order to enhance the resolution in the partial electron yield measurement. When the electron resolution is made infinitely poor, the convolution in Eq. (4) gives the same result as the normal total yield measurement.

We have thus shown that the utilization of partial yield techniques can result in line sharpening and that the method has the potential to reveal unresolved features of the photoabsorption spectrum. In general, however, the method may work for only core-to-bound excitations when the potential energy curves of the core-excited and final states are quite similar. Otherwise, the nominal kinetic energy of a resonant Auger transition, for which $\Delta\nu' = 0$, does not remain constant across the whole absorption feature. At the same time, the vibrational-lifetime interference would modulate so strongly the vibrational intensities and even the vibrational spacings, that the information obtained from the partial yield of resonant Auger electrons would no longer be comparable to normal photoabsorption.

Atoms always have energy levels without curvature and their resonant Auger decay shows linear dispersion. One might then think that a partial electron yield spectrum could help to resolve overlapping core-to-Rydberg excitations that are converging to an ionization limit. This, however, leads to electronic-state lifetime interference when different core-excited states can decay to the same final states through spectator and shake up/down transitions. The effect gives a nontrivial shape for the partial yield of resonant Auger electrons. Our method would therefore work only for atoms where the electronic interference is relatively weak, e.g., at excitations into adjacent Rydberg orbitals that have different l quantum numbers.

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