Observation of Autoionizing Resonances in Core-Electron Shakeup Spectra

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(Received 24 November 1986)

New phenomena observed in the shakeup satellite electron spectrum of Ne $1s$ are discussed. It is shown that for satellites lying above the shakeoff threshold, the structures observed correspond to autoionizing resonances. By use of high-resolution x-ray photoelectron spectroscopy the Fano profile of the $2s$-$3s$ lower shakeup satellite line is resolved for the first time. The Fano parameters for this line are determined to be $q=-2.2(2)$ and $\rho^2=0.35(5)$. The width of the resonance is 0.57(7) eV, i.e., almost a factor of 2 larger than the unperturbed linewidth.

PACS numbers: 32.80.Fb, 32.80.Dz

Electron spectroscopy studies of core-level satellites in atoms and molecules give important information on the dynamics of the photoionization process, e.g., of electron screening and electron correlation. The study of such satellites has also become a routine in applied spectroscopy.

It is interesting to note that very little has been reported on the linewidths and line profiles of the core-level satellites. It is normally assumed that these lines are broadened by the same mechanisms as the main lines, i.e., in free atoms the natural line shape should exhibit a Lorentzian profile possibly superimposed by a multiplet splitting. In molecules, vibrational and dissociative broadening give additional contributions. In a few cases, notably for the $4s$ and $4p$ levels in Xe and the neighboring elements in the periodic table[1-3] and for the $2p$ levels in Ni dihalides,[4] i.e., when the super-Coster-Kronig decay process is energetically possible, the effects of strong interaction between continuum states and discrete states have been shown to be important.

So far the study of autoionizing resonaces in atomic spectra has been performed with the use of variable-energy excitation sources and the resonances have been treated essentially as absorption phenomena. In this Letter we show that resonances also occur in x-ray photoelectron *emission* spectra from core levels. In core-electron spectra the terms shakeup and shakeoff are used to denote processes where the photoionization is accompanied by the simultaneous excitation of an electron to a discrete state (shakeup) or to a continuum state (shakeoff). These two channels may interact leading to resonances in the photoelectron spectrum even though the spectrum is excited by a discrete source.

The possibility of such an interaction mechanism is expected and special cases of interaction between discrete and continuum states in core-level electron spectra have earlier been treated.[1-3] In this report, our experimental conditions, however, permit the detection of this phenomenon as a general aspect of core-hole satellite electron spectra. Quantitative computational schemes to incorporate these interactions can now be tested.

The present results for Ne, which clearly demonstrate the interaction of continuum states with discrete shakeup states, serve as an illustration of a general effect which is present in all core-level satellite spectra and affects all satellite lines having excitation energies larger than the threshold for double ionization (the shakeoff threshold). By using high-resolution x-ray photoelectron spectroscopy (XPS), we have identified several autoionizing resonances in the double-ionization continuum associated with the Ne $1s$ electron line. From the line shapes it is possible to extract quantitative information about these resonances. In particular, we show that the shakeup core satellite associated with a final state dominated by the $1s2s(^3S)2p^63s(^2S)$ term interacts strongly with the $1s2s^22p^5\epsilon p(^2S)$ continuum. The corresponding electron line can be accurately fitted by a Fano line profile,[5] whereby the Fano parameters q and ρ^2 as well as the resonance position E_0 and the resonance width Γ can be determined.

The Ne $1s$ core-line photoelectron shakeup spectrum was studied with use of monochromatized x rays (1487-eV photon energy) for excitation.[6] The Ne gas was commercially obtained. In order to check for the effect of inelastic scattering of electrons in the sample gas, runs were made at different pressures and the inelastic scattering contribution could be subtracted. When we are measuring the intensity in the shakeoff continua it is also necessary for us to consider the spectrometer background which is due to scattering of electrons in the spectrometer walls. To a first approximation, this background was considered as a linear function that increases with increasing shakeup energy. A linear background was thus determined from the ends of the spectrum and was subtracted.

Figure 1 shows the total Ne $1s$ shakeup spectrum. It can be seen that this spectrum extends more than 150 eV above the main line. A large number of weak shakeup lines and also the shakeoff continua can be discerned. To discuss this spectrum we use the standard terminology. All $1s$ shakeup and shakeoff states have ^2S symmetry. These doublet states can, however, be formed by

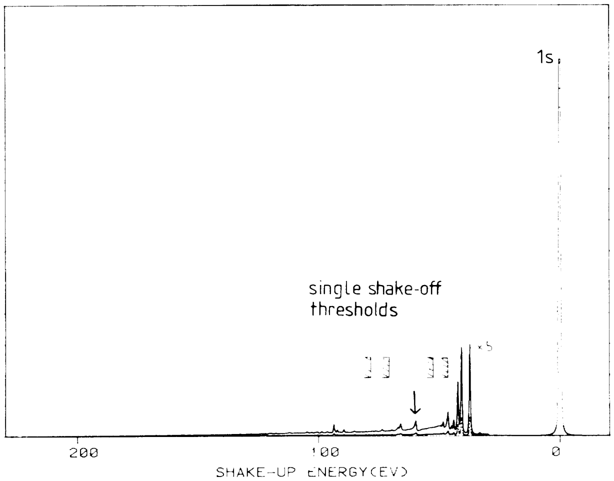

FIG. 1. The total single- and double-shakeup and -shakeoff spectrum associated with the Ne 1s core-electron line. The single-shakeoff thresholds are marked in the figure. The 2s-3s shakeup resonance is indicated by an arrow. The binding energy of the Ne 1s line is 870.21 eV (Ref. 7).

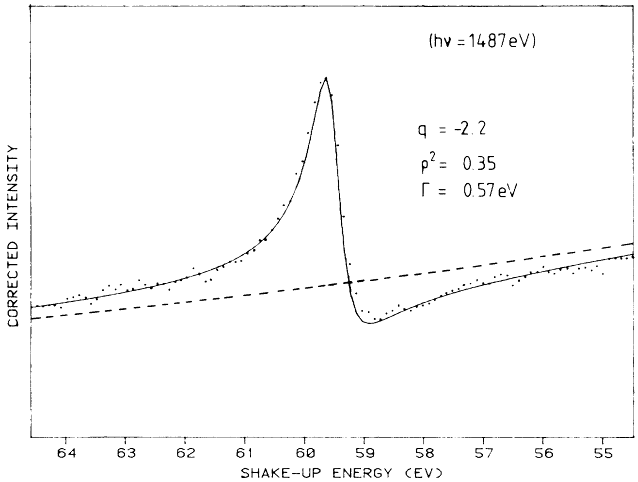

FIG. 2. The 2s-3s lower shakeup resonance. A small inelastic-scattering and spectrometer background has been subtracted. The dotted line indicates the unperturbed continuum intensity. The solid line represents a fit of a Fano line profile to the experimental points (see Ref. 10).

coupling of the 1s core hole to the 2s or 2p hole to form a triplet or a singlet parent term which then is coupled to the excited orbital to form a ^{2}S term. The triplet- and singlet-parent coupled ^{2}S terms interact and the states, dominated by the triplet and singlet parent terms are called the "lower" and "upper" states, respectively. Shown on the figure are the threshold energies for the $1s2s^22p^5(^{3,1}P)\epsilon p(^2S)$ single shakeoff processes at 46.7- (lower) and 51.4-eV (upper) shakeup energy and also for the $1s2s(^{3,1}S)\epsilon s(^2S)$ processes at 72.9 (lower) and 79.4 eV (upper). These energies can be obtained either from a Rydberg extrapolation among the shakeup states or from a combination of x-ray emission[7] energies and optical data.[8] There exists no controversy about the assignment of the most intense peaks in this spectrum.[9] The details of the assignment and determination of the shakeup thresholds will be given elsewhere. Here we will focus on one particular line, the line corresponding to a final state dominated by $1s2s(^3S)2p^63s(^2S)$. This state lies, as seen in Fig. 1, in the $1s2p^5(^{3,1}P)\epsilon p(^2S)$ shakeoff continua. The channels involved have the same symmetry and can therefore interact; the discrete state becomes an autoionizing resonance which has a Fano-type line profile. An enlargement of the interesting shakeup energy region is shown in Fig. 2.

Parameterized equations describing autoionizing resonances are developed by Fano,[5] Shore,[11] Starace,[12] and others. In the parametrization by Fano, the equation describing a single resonance line is given by

$$\sigma=\sigma_0\{\rho^2[(q+E)^2/(1+E^2)]+1-\rho^2\}, \tag{1}$$

$$E=(E^{\text{kin}}-e_0)/(\Gamma/2),$$

where E_0 is the unperturbed kinetic energy of the photoelectron from the discrete state, E^{kin} is the photoelectron kinetic energy, Γ is the width of the resonance, and q and ρ^2 are the so-called Fano parameters giving the shape of the resonance and the strength of the continuum, respectively.

The Fano parameter q is connected to the line asymmetry. A large q gives almost a symmetric Lorentzian line profile whereas a small q ($|q| \ll 1$) would give a dip in the continuum background. Equation (1) was fitted to the resonance shakeup line in Fig. 2. As can be seen from this figure the theoretical Fano profile gives a good description of the shape over the whole energy range. The fit in Fig. 2 determined the parameters E_0, Γ, q, and ρ^2. The Fano parameters $q=-2.2(2)$ and $\rho^2=0.35(5)$ were obtained. The negative value $q=-2.2$ reflects the very asymmetric profile. It should be pointed out that in lower resolution and signal-to-background this asymmetric broadening of the line is smeared out to a symmetric broad structure.

A detailed study shows that all the lines having a larger shakeup energy than 46.7, i.e., above the threshold for 2p-ϵp (lower) shakeoff, exhibit more or less resonance character, notably the 2s-4s upper, but also the 2s-3s upper and the 2s-4s lower lines. The first shakeoff threshold corresponds to the lower 2p-ϵp process, i.e., the $1s2s^22p^5(^3P)\epsilon p(^2S)$ term dominates. It is clear from Fig. 1 that some of the upper 2p-np shakeup states fall in this continuum and have a resonance line profile. A detailed study of all these lines will be given elsewhere.

The peak position at 59.67-eV shakeup energy and the resonance energy at 59.51 eV differ by as much as 0.16 eV. The width of the resonance is large, 0.57(5) eV, and has only a small contribution from the spectrometer resolution. With the consideration of the steep decrease of intensity to the right of the resonance peak in the experimental spectrum, it is evident that the spectrometer resolution is of minor importance for determining the width of the resonance since the fit is mostly determined by the flanks which are only to a small degree affected by the spectrometer function. The natural width of the Ne $1s$ line is 0.27 eV.[6,13] To our knowledge no calculations of the linewidths of the unperturbed $2s$-$3s$ shakeup states exist. However, for shakeup energies lower than 46.7 eV, i.e., in the region where no shakeoff process is energetically possible, we find that the natural linewidth of the largest two satellite lines associated with the $2p$-$3p$ shakeup process in Fig. 1 is 0.30(5) eV. This shows that the natural width of these states is about the same as the natural Ne $1s$ linewidth. Furthermore, for both $2s$ and $2p$ shakeoff states we know that the lifetime is larger than for the core $1s$ state in Ne.[7] From this we conclude that also the unperturbed $2s$-$3s$ shakeup states should have approximately the same or slightly smaller linewidths than the Ne $1s$ main line. Thus we conclude that the interaction with the shakeoff continuum has the effect of making the linewidth of the resonance approximately a factor of 2 larger than the unperturbed shakeup state.

Our high-resolution spectrum shows that it will be necessary to develop quantitative theoretical methods beyond the discrete shake-theory calculations[14] to give a full description of core-electron shakeup spectra. This is, however, not a trivial problem in our case since two shakeoff continua are involved and therefore multichannel interaction has to be considered. A possible theory for shakeup resonances could, e.g., take the proposals in a recent paper by Ohno and Wendin[15] as a starting point.

In conclusion, we find that, although we are using a discrete x-ray source to excite the electron spectra, autoionizing resonances are of importance in the shakeup spectra of core lines. In the case of the $2s$-$3s$ lower shakeup transition it has been possible to determine the Fano parameters of the resonance.

The authors want to thank Professor O. Goscinski for valuable discussions and J. O. Forsell and H. Rydåker for technical assistance. This work has been supported by the Swedish Natural Science Research Council.

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[10] The actual fit was made with use of the parametrized equation given by Shore which is easier to handle in a curve-fitting routine. The line was thus fitted by the equation

$$\sigma = C(E) + (B + AE)/(1 + E^2),$$

where E has the same definition as in Eq. (1). A, B, and $C(E)$ are the so-called Shore parameters. However, these parameters have dimension and therefore it is better, especially when the absolute cross sections are unknown, to calculate the corresponding Fano parameters:

$$q = [B \pm (A^2 + B^2)^{1/2}]/A,$$

$$\rho^2 = A/2qC(E_0).$$

The continuum strength is described by $C(E)$. We approximated this function as an exponential which increases with kinetic energy. This exponential is drawn as the dotted line in Fig. 2.

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