

Electronic state-lifetime interference observed at Ne K inter-resonance excitation

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Abstract

Electronic decay spectra of Ne, excited at the 1s threshold have been measured. Final states of the $2p^{-2}n'p$ configuration are reached via $1s^{-1}np$ intermediate states. Appreciable intensity from spectator shake transitions ($n \neq n'$) is found and the predictions of a simple intensity model are evaluated. The model reproduces the experimental results at on-resonance excitation. At inter-resonance excitation an apparent excitation energy dependence of the shake probability is accounted for by electronic state-lifetime interference theory.

For the first row elements core hole lifetimes are in the range of a few femtoseconds. A trivial consequence of this is the lifetime broadening in excitation and emission spectra. In addition, however, under special circumstances, information about the coherent nature of the excitation–emission process is revealed in the decay spectra. This is the case when the energy separation between core hole states in a system is of similar magnitude as the lifetime broadening. If these states have transition amplitudes to the same final state, their mutual interference may be observed in the decay spectra. This has earlier been demonstrated for small molecules, where the evolution of the nuclear wavefunction in the core hole state is reflected in the interference between vibrational substates [1,2]. We have pointed out that

monochromatic synchrotron radiation can be used to emphasize excitations, where interference effects are important also in cases where the core hole lifetime broadening is small relative to the energy spacing. At inter-resonance excitation, when the primary energy is tuned to spectral regions, where the Lorentzians of several states overlap, strong interference effects have thus been observed among the vibrational sublevels of the $C 1s^{-1}\pi^*$ state in CO [3,4].

There are several theoretical descriptions of the vibrational-lifetime interference effect [5–7] and the theory has also been generalized to include electronic state-lifetime interference [8]. The electronic decay of resonantly excited core hole states in rare gas atoms often includes shake processes [9]. In a simple picture the core electron, that is initially excited to the nl orbital, may be found in the $n'l$ ($n' \neq n$) orbital after the Auger decay. This means that the same final state can be reached via different core excitations, and state interference effects may hence be observed.

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In this Letter we present electronic deexcitation spectra excited in the energy range of the $1s^{-1}np$ ($n = 3, 4$) resonances in Ne. The on-resonance data confirm a simple shake intensity model based on the overlap between the orbitals [9] in the intermediate and the final state potentials. Interference effects are of minor importance here since the energy spacing between the states is large compared to the lifetime broadening. At *inter-resonance* excitation, between the $1s^{-1}3p$ and $1s^{-1}4p$ states, however, we observe interference effects, that we describe by a simple model, that combines the shake and interference theories.

The experiment was carried out at the soft X-ray undulator beamline BW3 [10] at the bypass at HASYLAB in Hamburg, using a double pass cylindrical mirror analyzer (commercial PHI 15-255 CMA) with the resolution set to 0.8 eV.

A high-resolution K absorption spectrum of Ne is shown in Fig. 1, together with arrows indicating the excitation energies chosen for the deexcitation spectra. The peaks are assigned to the $1s^{-1}np$ states ($n = 3, 4, 5$).

In Fig. 2 we show the decay spectra excited on the two first resonances. Excitation at the $1s^{-1}3p$ resonance we observe four final states characterized by emission lines at kinetic energies of 811.3, 807.5, 806.2 and 802.5 eV. The two peaks at the highest

energies are assigned to the $2p^{-2}3p$ configuration, split due to the 1D and 1S parental $2p$ coupling. This coupling does not, within the accuracy of the measurement, depend on the excited electron. The two low-energy peaks are associated with the $2p^{-2}4p$ configuration, i.e. the decay process involves a spectator electron shake-up.

Analogously, the peaks in the spectrum excited on the $1s^{-1}4p$ resonance are assigned to the 1D – 1S split $2p^{-2}3p$ (809.2 and 813 eV), $2p^{-2}4p$ (804.0 and 807.7 eV) and $2p^{-2}5p$ (802.1 and 805.8 eV) states. The peak appearing at 811.3 eV is due to the tail of the monochromator function exciting the $1s^{-1}3p$ state, leading to the same final state as the peak at 813 eV.

Such a ‘line doubling’ has been taken as an indication of the coherent nature of the excitation–emission process [11], but is merely a consequence of details in the monochromator function. With a perfectly narrow monochromator function this line would disappear in the spectrum.

It is obvious that transitions where the excited electron stays as a spectator during the decay as well as processes where the electron is shaken up and down contribute to the spectrum. Aksela et al. [9] have earlier concluded that the Ne $2p^{-2}4p$ states are reached with appreciable intensity from the $1s^{-1}3p$ state. To explain the low intensity of the $n = n' = 4$

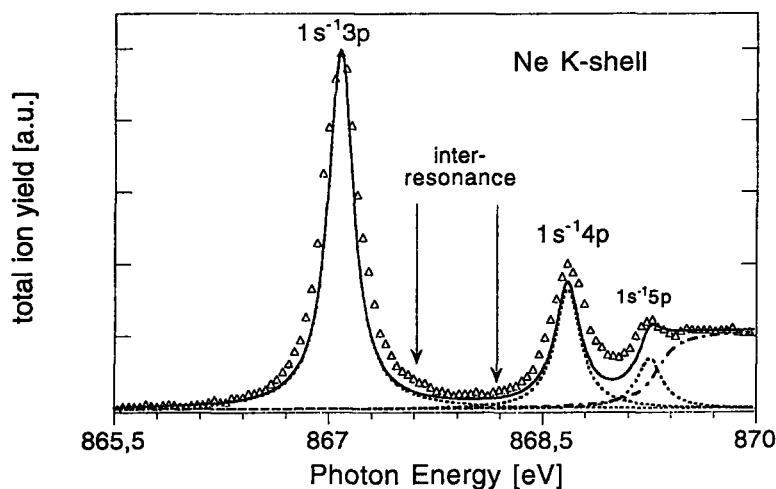


Fig. 1. The K-shell ion yield spectrum of Ne. The dashed lines refer to calculated intensities using a core hole lifetime-broadening (Γ) of 215 meV. The decay spectra in Fig. 2 have been excited on-resonance at 867.08 and 868.68 eV, the corresponding spectra in Fig. 3 are excited at 867.63 and 868.19 eV between the two absorption maxima.

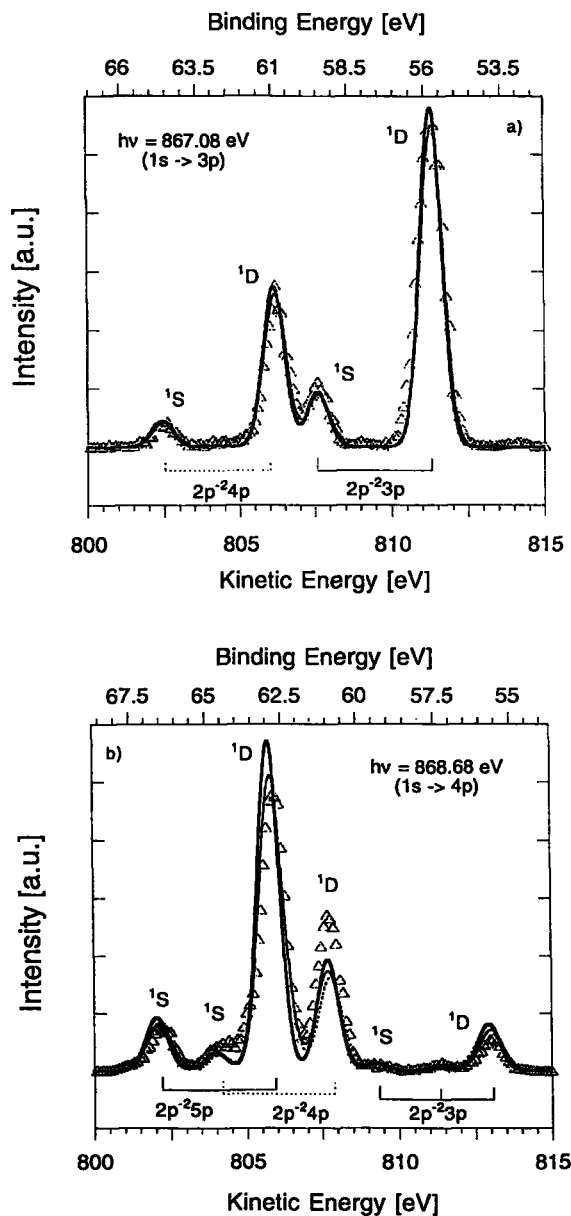


Fig. 2. Decay spectra excited on the $1s^{-1}3p$ and $1s^{-1}4p$ resonances ($h\nu = 867.08$ and 868.68 eV). The thin full line is the calculated spectrum according to Eqs. (4) and (5). Here a Voigt profile with 0.795 eV Gaussian and 0.10 eV Lorentzian widths assumed as the most realistic monochromator function has been used. The dashed line is the prediction when the interference is neglected. The thick solid line refers to the calculation in which the monochromator function has been modified to a rectangular shape with a fwhm of 0.4 eV convoluted by a Lorentzian of 0.10 eV. In all calculations we have used $\Gamma = 0.215$ eV. The calculated spectra are convoluted by a final electron spectrometer function assuming a Gaussian with a fwhm of 0.8 eV, respectively. The term symbols refer to the $2p^{-2}$ parental two-hole electron configuration.

spectator transition, they predicted a strong $n = 4 \rightarrow n' = 5$ shake-up probability. This prediction is confirmed by our experimental results, where the $2p^{-2}5p$ states are the strongest lines in the spectrum of Fig. 2b.

The final states involve two vacancies in the $2p$ orbital, one bound excited electron and one electron in the continuum. Because of the complexity of the states, it is difficult to calculate the decay intensity on a higher level of sophistication. We follow the model used by Aksela et al. [9], where the shake probability is associated with the sudden change experienced by the np electron at the time of the decay. The transition probability is then

$$I(1s^{-1}np \rightarrow 2p^{-2}n'p) \propto |T_{n,fr}|^2 |\langle np(i) | n'p(f) \rangle|^2, \quad (1)$$

where the first factor is the Auger decay probability calculated with frozen orbitals. The shake probabilities are determined from the overlap of the $|np(i)\rangle$ orbital in the intermediate state with the $|n'p(f)\rangle$ orbital in the final state. The wavefunctions were generated from a potential optimized with respect to the initial and final states, respectively [12]. In order to have states with different $np, n'p$ -spectator electrons orthogonal to each other, a common potential for all of them must be used. We determined self-consistent potentials for configurations with and without the spectator electron and found that the overlap, $\langle np(i) | n'p(f) \rangle$, depends sensitively on the self-consistency procedure. The matrix elements give best agreement with the experimental observation, when the spectator electron is included in the self-consistent scheme. It should be pointed out that the problem of determining highly excited states self-consistently needs further investigation.

Eq. (1) evaluated with orbitals optimized in the presence of an excited $3p$ electron predicts the measured shake probabilities with high accuracy (Fig. 2). The prediction that the $1s^{-1}4p \rightarrow 2p^{-2}5p$ shake-up transition is more intense than the $1s^{-1}4p \rightarrow 2p^{-2}4p$ spectator transition is confirmed. The theory slightly underestimates the probability that the electron stays in the $4p$ orbital during the decay.

The simple and lucid picture described by Eq. (1) involves, apart from the one-electron approximation, several assumptions regarding the time development

of the excitation–emission process. Especially, it assumes that the excitation (suddenly) prepares a fully developed core hole “eigenstate” that undergoes a sudden decay. Such a model is not applicable when we consider inter-resonance excitation.

In Fig. 3 we show the decay spectra excited in the region between the $1s^{-1}3p$ and $1s^{-1}4p$ resonances. The population of the final states varies for the trivial reason that the cross sections for the $1s^{-1}3p$ and $1s^{-1}4p$ transitions vary with energy, but we note that there also is an *apparent excitation energy dependence of the shake-up probability*. Especially, we note that the $2p^{-2}4p$ final states are reached with the largest probability at inter-resonance excitation, whereas they have less intensity than the $2p^{-2}5p$ final states at $1s^{-1}3p$ as well as $1s^{-1}4p$ on-resonance excitation. From the intensity of the direct photoemission peak we estimate the valence shake-up intensity in the energy region to be 40 times weaker than the measured structures at inter-resonance excitation, and hence this excitation channel can be safely neglected. Below we will discuss this behavior in terms of electronic state-lifetime interference.

It has been shown that vibronic and electronic state-lifetime interference can be treated on an equal footing [8]. Assuming that no energy constraint is given by the exciting radiation, a final state can be reached via resonances with various intermediate states with the intensity:

$$I(E_{exc}) \propto \left| \sum_i \frac{\langle \psi_f | T_2 | \psi_i \rangle \langle \psi_i | T_1 | \psi_0 \rangle}{E_e - (E_i - E_f) + i\Gamma/2} \right|^2. \quad (2)$$

ψ_0 , ψ_i , and ψ_f are the wavefunctions of the ground, intermediate and final states, respectively, Γ is the lifetime broadening of the intermediate state, T_1 is the dipole operator and T_2 is the Coulomb operator. E_e , E_i and E_f are the energies of the emitted electron, the intermediate states and the final state, respectively.

For the case where the energy of the intermediate states is constrained by the monochromator function, $M(E_{exc})$, we rewrite Eq. (2) using energy conservation and the assumption that the final state broadening is negligible:

$$E_e = E_{exc} - (E_f - E_0). \quad (3)$$

Here E_0 is the ground state energy and E_{exc} is the excitation energy. The intensity for the population of the final state is then

$$I(E_{exc}) \propto M(E_{exc}) \left| \sum_i \frac{\langle \psi_f | T_2 | \psi_i \rangle \langle \psi_i | T_1 | \psi_0 \rangle}{E_{exc} - (E_i - E_0) + i\Gamma/2} \right|^2 \quad (4)$$

We have successfully used an analogous equation to describe spectra involving vibrational interference effects in molecules [1,3,13]. Recently, Pahl et al. [14] derived the excitation dependence of the decay intensity as expressed by this time-independent formula in general to be exact for this kind of decay experiment.

It should be noted that for one intermediate state Eq. (4) simply is a Lorentzian multiplied by the monochromator function. The width of $I(E_{exc})$ in the limit of narrow $M(E_{exc})$ and large Γ is fully determined by $M(E_{exc})$. This “elimination of the lifetime broadening” and the linear variation of E_e with E_{exc} (Eq. (3)) has often been taken as an indication of the one-step nature of the excitation–emission process [15]. Such observations are, however, only consequences of the conservation of energy (for isolated systems) and have no implications for the excitation–emission dynamics [16].

Vibrational-lifetime interference can be evaluated in a time-dependent framework [14,17], where the absorption of the photon creates a wavepacket which, while developing, is decaying via Auger emission. The excitation, the time evolution of the intermediate state and the decay are intimately connected processes that cannot be separated. This total time evolution is in the present time-independent formalism reflected in the interference effects.

To account for the interference effects we evaluate Eq. (4) with an expression inspired by Eq. (1):

$$\langle \psi_f | T_2 | \psi_i \rangle = T_{n,fr} \langle n p(i) | n' p(f) \rangle \quad (5)$$

In Figs. 2 and 3 the results of the analysis according to Eqs. (4) and (5) are shown together with the experimental spectra. The dashed line shows the intensities calculated without interference contributions. The thin solid line is the result of including the interference effects and using a monochromator function as a Voigt profile with 0.795 eV Gaussian and 0.10 eV Lorentzian width. Such a Voigt-type

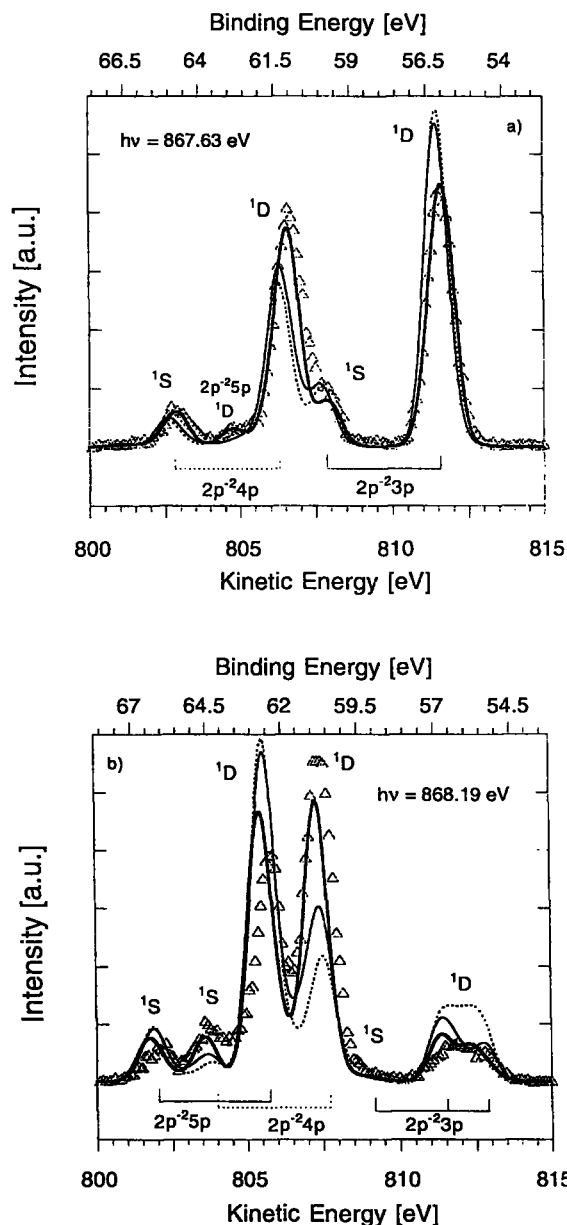


Fig. 3. Decay spectra excited at inter-resonance, according to the arrows in Fig. 1 ($h\nu = 867.63$ and 868.19 eV). The same theory is used as for the spectra in Fig. 2.

$M(E_{exc})$ is realistic for small slit widths and the resolution is consistent with the measured absorption spectrum. We see that the inclusion of interference is unimportant for the spectra excited on resonance, but

is essential to understand the spectra excited between the resonances.

For a quantitative comparison with theory full knowledge of the monochromator function is necessary. We note that a 0.4 eV wide rectangular function convoluted by a 0.10 eV Lorentzian gives an almost perfect agreement with the experimental data (thick solid line in Figs. 2 and 3). Thus, the experimental results clearly demonstrate the electronic state-lifetime interference effects. The quantitative accuracy of the analysis is, however, limited by the ambiguity in the form of $M(E_{\text{exc}})$.

The net interference intensity contribution due to interference is zero integrated over all decay channels [18]. Also for measurements in restricted energy regions, as in the present case, this sum rule appears to hold. The interference only redistributes intensity in the spectrum.

We note again that the whole time evolution of the wavefunctions [14,17] during the scattering process is reflected in the lifetime interference effects as described by Eq. (4). The substitution of matrix elements evaluated using fully relaxed frozen intermediate states (Eq. (5)) can be questioned, however, when the time development is important. In the limit of large Γ the scattering process cannot be well-described in terms of fully relaxed intermediate states.

In conclusion we have presented the electronic decay spectra of Ne, excited around the 1s threshold. At on-resonance excitation we identify spectator as well as shake processes in the decay. The intensities are well reproduced within a simple model based on the overlap of the np orbitals in the intermediate and the final state potential. At inter-resonance excitation an apparent excitation energy dependence of the shake-probability is accounted for by electronic state-lifetime interference theory.

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