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On the spectral lineshapes, lifetimes and deexcitation processes of autoionizing states produced in inelastic ion–surface collisions

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Abstract. The natural lineshapes of peaks in electron spectra due to decay of autoionizing states of Ne, formed in collisions of Ne with Mg and Al solid targets, are modelled. The modelling takes into account the level shifts of the excited and ionic states of the atom in front of the surface and various resonant and Auger capture and loss processes. It is shown that rather complex lineshapes may be expected. The electron spectrum will generally possess a peak at energies in the vicinity of that corresponding to autoionization of a free atom, as well as a high-energy tail and secondary maximum. It is suggested that a structure observed at 22.2 eV in the experimental Ne** electron spectrum is just such a secondary maximum associated with the decay of the Ne** $^3P\ 3s^2$ near the metal surface. The effects of varying the model lifetimes, electron capture and deexcitation rates are discussed.

1. Introduction

A number of recent studies [1–5] have focused on the production of doubly excited autoionizing states of inert gas atoms in collisions with metal targets. These states are a signature of inelastic violent 'binary' collisions of incident and target atoms. The study of their formation is interesting both from the point of view of the study of mechanisms of excitation and also of various electron transfer processes which are involved in their production. In this paper we shall consider some as yet unexplored characteristics of the formation of these states in keV collisions of Ne ions.

Experimentally these are observed as well defined structures or peaks in the electron spectra, which are superposed on a continuous background due to potential and kinetic electron emission. The electron energies at which they appear are found to be close to the ones expected for decay of these states for free atoms. Shifts from these positions have been attributed to kinematic effects [1–5], i.e. due to emission from a moving source: a scattered atom, rapidly receding from the surface. Rather strong variations in the shapes of these peaks have been observed, when the collision energy and especially observation angle is varied [2]. Thus these peaks are generally asymmetric, with low- or high-energy tails, depending upon whether the observation angle as measured with respect to the incident ion beam direction is small or large respectively. This behaviour has been related to the characteristics of the ion angular distributions [2, 3], which extend to rather large scattering angles and are characterized by large energy losses. Preliminary calculations [2] of the lineshapes, assuming a delta function *natural* lineshape and taking into account kinematic and apparatus

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broadening effects, have been found to reproduce qualitatively these features. The above analysis showed [4] that there exists the very interesting possibility of developing a Doppler tomographic method of extracting scattered particle angular and energy distributions from these spectra. This technique is not yet fully developed and there subsist some problems. Thus existing calculations could not account for a high-energy component in the line profile, which extends beyond the maximum electron energy as expected from the kinematic shift related to the highest-energy scattered atoms. This high-energy half width at half maximum (HWHM) is of the order of a few tenths of an eV. The shape of the experimental spectra also suggest the existence of high-energy tails of these peaks extending up to a few eV.

Another important aspect of this problem lies in that complex lineshapes significantly complicate identifications of peaks in the electron spectra. The correct description of collisional mechanisms is hindered by such uncertainties. An example are recent works on Ne scattering, where some structures remained unexplained. In this specific case the spectrum is mainly dominated by peaks due to the Ne^{**} ^3P $3s^2$ and ^1D $3s^2$ states lying at electron energies of 20.35 eV and 23.55 eV respectively [6]. There also exist some additional small structures at higher energies which may be assigned to higher-lying states such as the $(2s^22p^4)^3P$ $3p^2$ state or states of the $2s^22p^3nln'l'$ configuration etc (see e.g. [5, 7] for a more complete list). A curious feature or bump was observed [5, 7] at an energy of 22.2 eV, which was tentatively assigned [7] to the $2s2p^63s$ state, though the excitation of a such a state with with an inner vacancy seems unlikely. A previous assignment to the $2p^43s3p$ state seems unreasonable (see also [7]), because the electron energy corresponding to this state should be 22.9 eV, as found in gas phase experiments [6]. An alternative explanation could be that this bump is due to a feature in the angular distribution of scattered particles [2].

Basic information, which was lacking until now, was the absence of at least some qualitative indications about the characteristics of *natural* lineshapes. It is now well known that in doubly charged ion scattering [8, 9] on metals, electron spectra display broad peaks due to autoionizing states, which in this case are formed on the *ingoing* trajectory and result from successive capture and loss processes, *before* the ion reaches the surface. The energy position of these peaks is not the same as in the above *scattered* ion case but is higher, due to level shifts near the surface. This shift also explains their large widths. The natural lineshapes have been modelled in this case in some detail [8, 9]. A preliminary calculation [9] of the shape of the peak due to an autoionizing state for an atom leaving the surface indicated the possible existence of a rather complex, structured, line profile.

In this paper we present an analysis of some characteristics of lineshapes, which may be expected from general considerations regarding level shifts and various capture, loss and deexcitation processes near the surface.

2. The model

The doubly excited Ne^{**} atoms are formed as a result of a violent, small impact parameter collision of an incident Ne ion or atom with a surface atom. On the basis of general considerations regarding excited state formation in gas phase collisions, it is expected that this binary collision will lead to the dominant formation of states of the $2p^4(^1D)$ Ne^{2+} core configuration. The exact nature of the excited species formed in this collision is not known. Very close to the surface, the energy levels of most excited states will lie above the Fermi level and are hence autoionizing. As the excited particle: excited atom or singly or doubly charged ion leaves the surface, we have to consider a series of Auger and resonant decay and capture processes, which may lead to the experimentally observed final

state distribution of Ne^{2+}, Ne^{+*}, Ne^{*}, Ne^{+}, Ne. The experimentally observed, dominance of the autoionizing states of the triplet core configuration has been assigned to Auger deexcitation in the quasimolecule formed during the binary collision [1–4, 7] and also to 'atomic' core rearrangement induced by Auger deexcitation ($2p^4(^1D)nln'l' \rightarrow 2p^4(^3P)nln'l'$, or Ne^{2+} $2p^4(^1D) \rightarrow Ne^{2+}$ $2p^4(^3P)$) [10] as well as to resonant autoionization [11] into the metal $+Ne^{2+}(2p^4\ ^3P)$ continuum near the surface, followed by sequential resonant electron captures (i.e. Ne^{+*} $2p^4(^1D)nl \rightarrow Ne^{2+}$ $2p^4(^3P)$ + metal, Ne^{2+} $2p^4(^3P) + e^- \rightarrow 2p^4(^3P)nl$, etc) (see also [12]).

Because of the complexity of the problem, we adopt a *model* simplified reaction scheme involving a series of electron capture and loss processes schematized in figure 1. We replace the actual manifold of levels by the lowest terms and here we shall only consider the Ne^{+*} $2p^4(^3P)3s/3p$ and Ne^{**} $2p^4(^3P)3s^2/3p^2$ excited states, in order to illustrate different cases of line profiles. We also neglect fine-structure splittings. This in practice will produce an additional overall broadening of lineshapes as may be seen in gas phase experiments [6], where for instance a deconvolution of splitting of the ^1D $3s^2$ experimental lineshape of 0.097 eV was performed. Here we shall discuss significantly larger broadening effects.

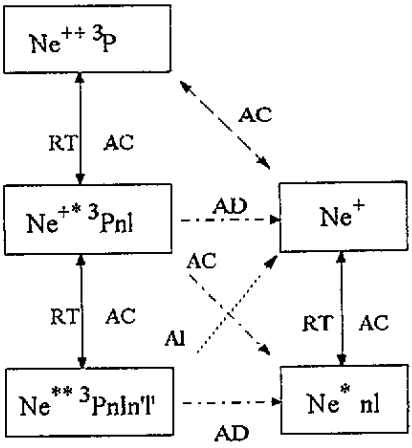

Figure 1. Electron loss and capture scheme between various Ne^{2+}, Ne^{+}, Ne states. The various Auger capture (AC), Auger deexcitation (AD), resonant transfers (RT) and autoionization (AI) channels between states are indicated. The excited states actually considered are given in the text.

We assume that the excited species start out at a distance of two atomic units from the image plane and consider their ejection into a range of θ_{ex}, with E_{ex} corresponding to energy losses in single-scattering conditions. This choice of the starting distance was not found to affect the lineshapes.

As in our previous work [9, 11], we use a numerical model built along the lines of [8]. Figure 2(a). shows the metal + atom/ion states corresponding to the scheme in figure 1. The position of the levels in front of the surface was modelled as described in some detail in [8] and is given mainly by the image potential at large distances, whereas at small distances screening effects are taken into account. As may be seen for distances smaller than ~2.2 au the $(^3P)3s^2$ state lies above the Fermi level and can autoionize to give the Ne^{+*} $(^3P)3s$ state. In the range of distances considered the ^3P 3s state lies below the Ne^{2+} state. On the other hand, the higher-lying ^3P 3p Ne^{+*} state can autoionize into the continuum corresponding

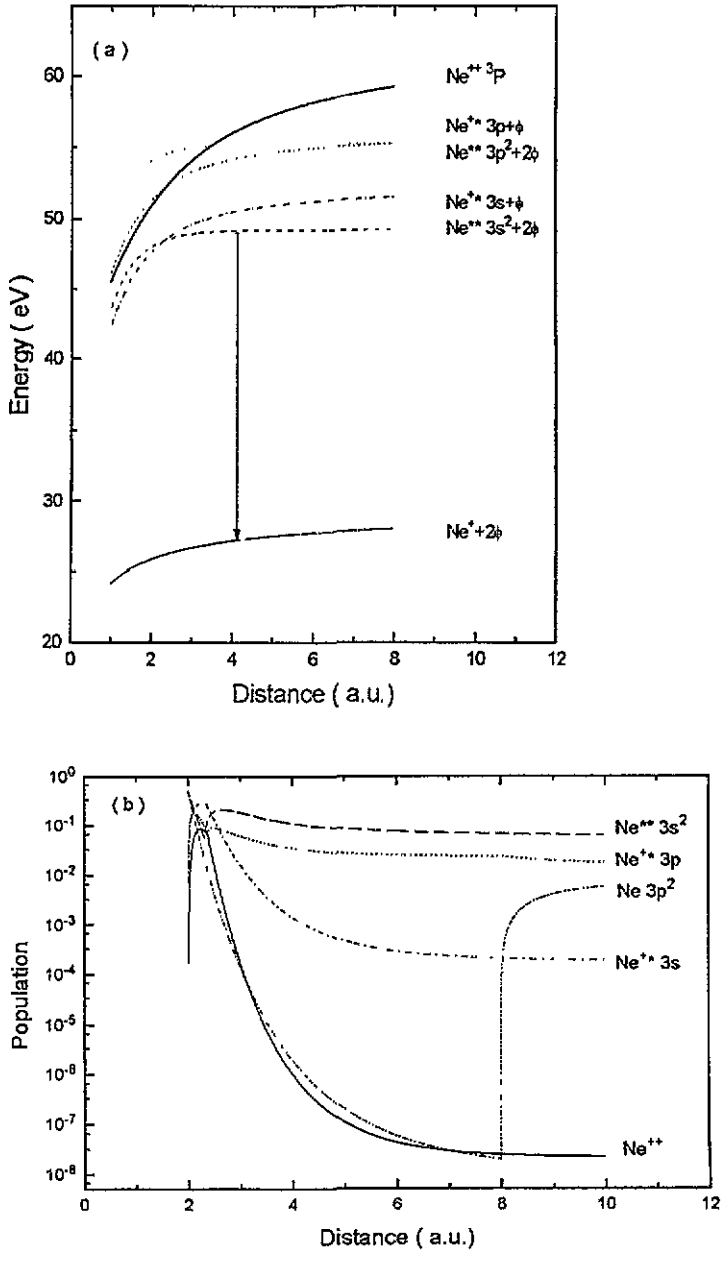

Figure 2. (a) Potential energy diagram of the Ne–Mg system used in the calculations, represented here for electrons at the Fermi level. The states are identified on the right of the diagram. The thick line represents the Ne^{2+} + metal continuum. (b) Populations of the various states as a function of the distance from the image plane ($\theta_{ex} = 24°$, $E_{ex} = 1.72$ keV).

to metal $+Ne^{2+}$ for distances smaller than 2.2 au. The $(^3P)3p^2$ remains autoionizing for distances as large as 8 au, which as shown previously [11] explains the small probability of its production.

We solve a set of coupled differential equations for the distance-dependent populations

of the various levels.

$$\frac{dN_i}{dz} = \sum_{i \neq k} (G_{ki}(z)N_k(z) - G_{ik}(z)N_i(z))/v_\perp(z)$$

where $G_{ik}(z)$ are the probabilities for transition between i and k states and $v_\perp(z)$ is the perpendicular velocity. We assume that resonant and Auger transitions are caused by the overlap of the wave functions of the electron in its initial and final state and that $G_{ik}(z)$ is determined by the asymptotic behaviour of the wave functions. For resonant electron transfers (and resonant ionization)

$$G_{ik}(z)_{RT} = C_{RT}\rho(E)e^{-(\sqrt{2E(z)})z}$$

where $E(z)$ is the binding energy, C_{RT} is an adjustable parameter, and $\rho(E)$ is the metallic density of states (DOS), which is normalized to unity. The parameters chosen subsequently should be related to this normalization. For the case of resonant ionization $\rho(E) = \rho(\varepsilon_F)$. For Auger capture and deexcitation $G_{ik}(z)$ is defined as an integral over the binding energies of metal electrons in the band,

$$G_{ik}(z) = \int_{\varepsilon_{min}}^{\varepsilon_F} \rho(E)C_{AC}\, e^{-\gamma(z)_{ACZ}}\, dE_b$$

$$\gamma(z) = \left(\frac{1}{2\sqrt{2E_b(z)}} + \frac{1}{2\sqrt{2E_a(z)}}\right)^{-1}$$

where E_a is the recombination energy of the atomic electron. We also consider Auger capture into excited states and hence the lower limit in the above integral is not necessarily zero. In case of the filling of the inner 2p hole in neutralization and deexcitation, E_a was taken as the ionization potential of the atom. C_{AC} is an adjustable parameter.

The autoionization of the doubly excited atom into the ground state of the ion is assumed to be given by a distance-independent parameter C_{AI}. A jellium band structure is considered. For Mg the workfunction ϕ was taken to be 3.64 eV and the Fermi energy $\varepsilon_F = 7.1$ eV. For the Al target $\phi = 4.25$ eV and $\varepsilon_F = 11.7$ eV. No attempt at deriving the values of parameters from any fitting procedure was made. Most parameters were equated for simplicity and the following set was initially used as in our previous papers [9, 11] (in atomic units):

(i) Auger capture ($Ne^{2+} \rightarrow Ne^+$ and $Ne^+ \rightarrow Ne^0$): 0.4;

(ii) Auger deexcitation: 0.2;

(iii) resonant neutralization and ionization: 0.05 (note that $0.05\rho(\varepsilon_F) \cong 0.3$);

(iv) $C_{AI} = 0.0005$ au as for Ar^{**} [8] and corresponds to a lifetime (τ) of about 5×10^{-14} s.

Calculations were performed for 2 keV Ne incident at a 6° grazing angle to the surface, assuming that the collisionally produced state distribution is (a) 50% $Ne^{**}3s^2$ and 50% $Ne^{**}3p^2$, (b) 50% $Ne^{+*}3s$ and 50% $Ne^{+*}3p$ and (c) 100% Ne^{2+}. Results of simulations of these lineshapes for the above and other parameters are presented in the following.

3. General characteristics of lineshapes

Results of the calculation of the populations of the various levels as a function of atom–surface distance, using the set of parameters given above and assuming an initial population of 50% $Ne^{**}3s^2$ and 50% $Ne^{**}3p^2$, are schematized in figure 2(b) for 2 keV Ne incident

at 6° grazing angle to an Mg surface and scattered through 24°. The exit angle is then of 18° and the final energy is 1.72 keV. Note that the experimentally determined maximum in scattered ion distribution for the above conditions of incidence lies at a 20° scattering angle [3].

As may be seen in figure 2(b) the initial population of Ne^{**} is initially strongly attenuated through resonant ionization leading to the production of Ne^{+*} and Ne^{2+}. The final production of Ne^{**} always relies on electron capture processes. For this reason, for a given set of parameters, the initial state distributions do not affect the spectral lineshapes.

Near the surface the Ne^{**} population can be attenuated by Auger deexcitation leading to Ne^{*}. The lineshapes of the peaks due to Ne^{**} are determined by the population of the Ne^{**} excited state at various atom–surface distances and the energy separation of the Ne^{**} and Ne^{+} levels.

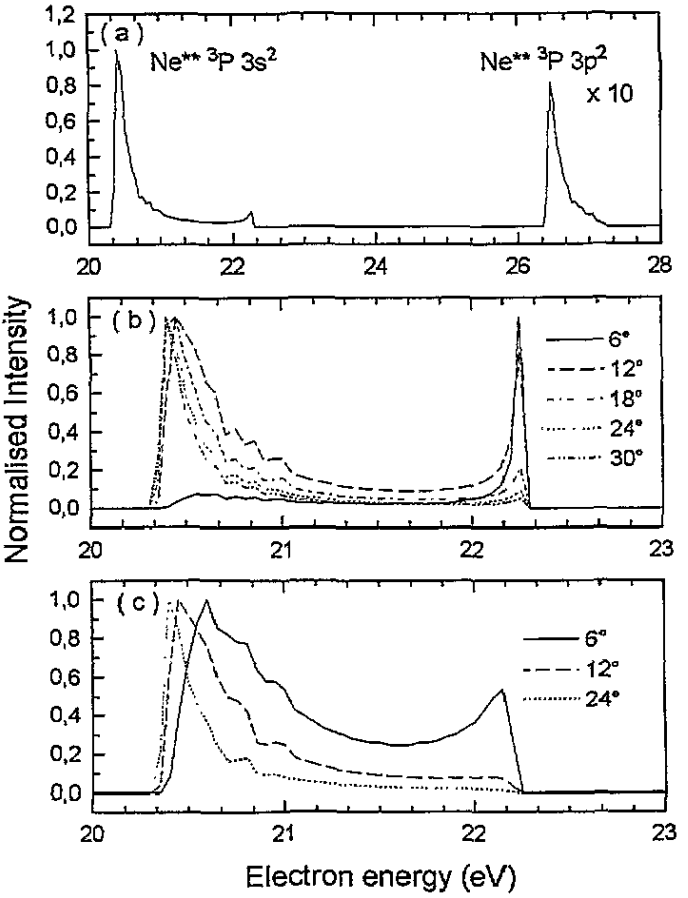

Figure 3. (a) Lineshapes due to autoionization of the Ne^{**} $2p^4(3P)3s^2$ and $3p^2$ states. Mg target. (b) Scattered atom exit angle dependence of the lineshape of the Ne^{**} $2p^4(3P)3s^2$ state. Mg target. (c) Scattered atom exit angle dependence of the lineshape of the Ne^{**} $2p^4(3P)3s^2$ state. Al target.

Figure 3(a, b) shows the calculated lineshapes for the $3s^2$ and $3p^2$ states, for the above values of the parameters and for various exit angles. As may be seen both peaks have a sharp

cut-off at small electron energies, close to the 20.35 eV and 26.7 eV position, corresponding to the autoionization of a free atom. On the other hand they have tails extending to high energies. In case of the $3s^2$ state this tail extends up to about 22.3 eV, corresponding to the maximum energy separation of the Ne^{**} and Ne^+ levels, for an atom-metal distance of about 2.2 eV, when the Ne^{**} state can ionize into the continuum $Ne^{+*}3s$ + metal. In the case of the $3p^2$ state, resonance ionization occurs at much larger distances, where the separation of the $Ne^{**}3p^2$ and Ne^+ levels is not altered as significantly as in the case of the $3s^2$ state and the corresponding tail is short.

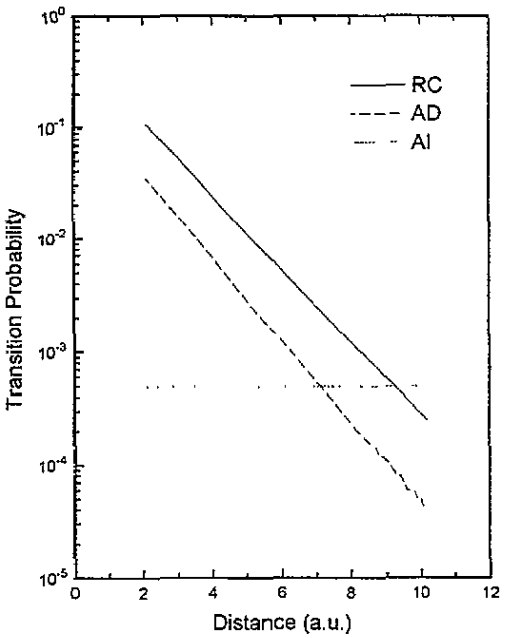

Figure 4. Resonant capture (Ne^{+*}–Ne^{**}) and Auger deexcitation (Ne^{**}–Ne^*) probabilities as a function of atom–surface distance. The distance-independent autoionization probability is also indicated.

A very specific feature of the $3s^2$ state lineshape is the secondary maximum at about 22.2 eV. This maximum is more pronounced for small exit angles with respect to the surface. Its origin may be sought in the variation of the population of the state as a function of distance. Close to the surface the population initially decreases rapidly because of Auger deexcitation, as may be seen from the relevant capture and deexcitation probabilities shown in figure 4. At larger distances it is determined only by autoionization. The secondary maximum arises from autoionization close to the surface, where the population is large and the $Ne^{**} - Ne^+$ energy separation is also large. At intermediate distances ($z < 10$ au) the population has decreased substantially, but the $Ne^{**} - Ne^+$ separation is still significantly larger than its asymptotic value. Decay in these conditions is responsible for the intermediate, tail portion of the peak. The main portion of the peak, i.e. the region from the maximum to about 21 eV, is similar to that of the $3p^2$ state and is determined by decay at large distances from the surface (tens of au). The shape of the peak in this region is thus determined by the autoionization lifetime of Ne^{**}.

In general, the lineshape obviously depends on the time spent in a given region of atom–surface distances. This effect determines its dependence on the exit angle and hence the

perpendicular velocity. For more grazing exit angles, i.e. for small perpendicular velocities, decay occurs closer to the surface and the spectra are broader than at larger exit angles (figure 3(b)). In these conditions the secondary maximum is also more pronounced and can be the dominant feature of the spectrum. The relative intensity of this maximum gives a measure of the efficiency of Auger deexcitation. For exit angles greater than about 18 degrees, the spectra are fairly narrow. For angles in the vicinity of the maximum of the experimental Ne^+ angular distribution, the width at half maximum of the peak in figure 3 is of the order of 0.3 eV. This value appears in reasonable agreement with the order of magnitude of the experimentally determined high-energy part of the peaks, which cannot be accounted for by kinematic effects. However it should be born in mind that the calculated spectra can not be directly compared with experiment, because the experimental ones correspond to a sum over the scattered Ne** angular distribution, which is not known at present.

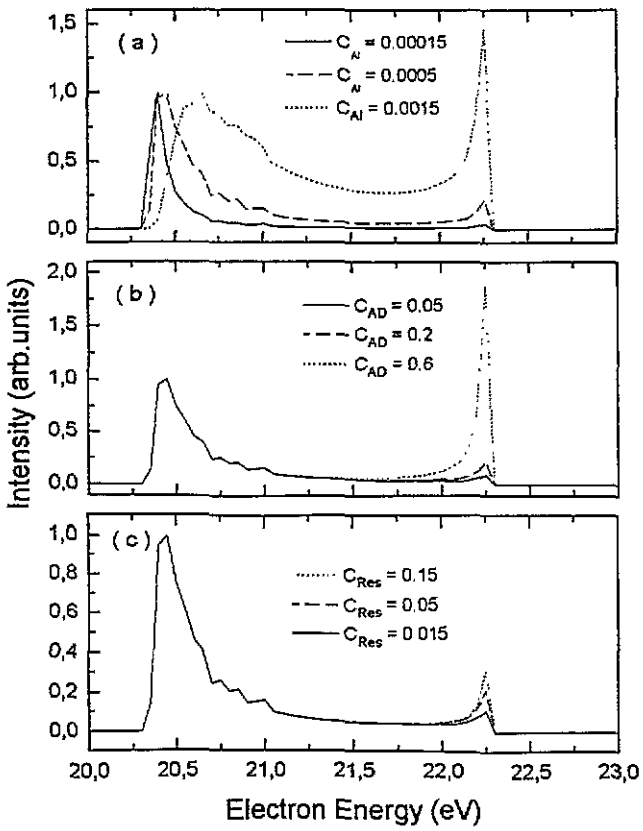

Figure 5. Effect of the change in (a) lifetimes, (b) Auger deexcitation and (c) resonant capture rates on the lineshape of the electron peak due to Ne** $3s^2$.

Figure 3(c) illustrates the exit angle dependence for 2 keV Ne ions incident at 6° on an Al surface. The spectra are in general similar to those for the Mg target.

This analysis thus shows that quite complex natural lineshapes may be expected. A noteworthy feature is that the secondary maximum at 22.2 eV could be responsible for the structure in the experimental spectra observed at this energy [5, 7].

4. Effects of lifetime, capture and deexcitation rates

In this section we examine the effect of changes in lifetime, resonant capture and Auger deexcitation rates on the lineshapes for scattering on Mg.

Figure 5(a) shows lineshapes calculated using different values for the autoionization rate. As may be expected, for long lifetimes ($C_{AI} = 0.000\,15, \tau = 1.5 \times 10^{-13}$ s) the spectrum turns out to be quite narrow and peaks very close to the position corresponding to the electron energy for the autoionization of a free atom. The high-energy tail subsists, but is of much smaller intensity. The peak at 22.2 eV essentially disappears. For a shorter lifetime ($C_{AI} = 0.0015, \tau = 1.5 \times 10^{-14}$ s), the spectrum is very broad, because decay occurs close to the surface. Also the 22.2 eV peak becomes very prominent. In this simulation we have assumed that the autoionization rate itself does not depend on the proximity of the surface. It is qualitatively clear that if this rate were to increase near the surface, it would lead to an enhancement of the 22.2 eV peak region.

Figure 5(b) illustrates the effect of changing the Auger decay rate. The low-energy part of the spectrum does not change, but an increase of the Auger decay rate induces an increase in the secondary 22.2 eV maximum.

The autoionization and Auger decay rates are not the only factors affecting the spectral lineshape. The situation is more complex and changes in the resonance capture rate by Ne^{+*} ^3P 3s leading to Ne^{**} ^3P $3s^2$ also induce a change in the form of the spectrum. This is summarized in figure 5(c). The low-energy part of the spectrum remains unchanged, but an increase in the electron capture rate leads to an increase of the secondary maximum at 22.2 eV.

5. Conclusions

The natural lineshapes of peaks in electron spectra due to decay of autoionizing states of Ne, formed in collisions of Ne with Mg and Al solid targets are modelled. The modelling takes into account the level shifts of the excited and ionic states of the atom in front of the surface due to image potential and screening effects and various resonant and Auger capture and loss and deexcitation processes. It is shown that rather complex lineshapes may be expected. The electron spectrum will generally posess a peak at energies in the vicintiy of that corresponding to autoionization of a free atom, as well as a high-energy tail and secondary maximum. The secondary maximum, associated with decay near the surface, is more pronounced for atoms scattered close to the surface, i.e. in conditions when the exit perpendicular velocity is small. It is suggested that the structure observed at 22.2 eV in the experimental Ne^{**} electron spectrum is just such a secondary maximum associated with the decay of the Ne^{**} ^3P $3s^2$ near the metal surface. The effect of varying the model lifetimes, electron capture and deexcitation rates are discussed. *Ab initio* calculations of the various capture, loss and deexcitation rates and of the energy levels of the Ne^{**} and Ne^+ states close to the metal surface would be most useful for a better quantification this problem.

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