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LETTER TO THE EDITOR

Electron impact ionization of Ca^+

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Abstract. We have carried out a number of close-coupling calculations for the electron impact excitation of the $3p^5 3d4s$ configuration of Ca^+ using the *R*-matrix method, so as to determine the indirect contribution to the ionization of Ca^+. We find that the large resonance features primarily due to capture into the $3p^5 3d^2 4s$ configuration, present when only the ^4P and the two ^2P terms of the $3p^5 3d4s$ configuration are included in the continuum close-coupling expansion, disappear when all nine terms of this configuration are included. The resulting ionization cross section is in reasonably good agreement with experiment over the energy range where dielectronic capture–autoionization features could be expected and resolves a long-standing disagreement between theory and experiment.

One of the first experiments to show the importance of excitation–autoionization in electron impact ionization was carried out by Peart and Dolder (1975) on Ca^+. The experiment showed a very large excitation–autoionization contribution with no major resonant features. More recently, Peart *et al* (1989) performed a much higher resolution experiment (~0.1 eV) and obtained essentially the same result, although a number of very small features were observed. This contrasts sharply with the theoretical picture.

Burke *et al* (1983) carried out a close-coupling calculation using the *R*-matrix method for excitation to the $3p^5 4s^2\ ^2P$, $3p^5 3d(^3P)4s\ ^{2,4}P$ and $3p^5 3d(^1P)4s\ ^2P$ terms, and obtained a cross section dominated by a large feature (~5 eV FWHM) which they identified as being due to dielectronic capture into the $3p^5 3d^2 4s\ ^{1,3}F$ terms of Ca followed by autoionization to autoionizing terms of Ca^+, which then autoionize to Ca^{2+}. Subsequently, Griffin *et al* (1984) carried out a distorted-wave calculation and showed that significant contributions to ionization come from all nine terms of the $3p^5 3d4s$ configuration, that the Auger yield departs significantly from unity for several of those terms and that there is a large term-dependent effect due to the 3d orbital in the $3p^5 3d(^1P)4s\ ^2P$ term being quite different from that in the remaining terms. However, their calculation did not include contributions from dielectronic capture followed by *sequential autoionization of two electrons*.

Later, Pindzola *et al* (1987) performed a term-dependent close-coupling calculation, still including only the two ^2P and the ^4P autoionizing terms of $3p^5 3d4s$; however, they used a 3d′ orbital for the $3p^5 3d'(^1P)4s\ ^2P$ term which was determined from a Hartree–Fock (HF) calculation for that specific term and was quite different from, and not orthogonal to, the 3d orbital employed for the $3p^5 3d(^3P)4s\ ^{2,4}P$ terms. They did not force orthogonality between the continuum orbitals and the bound orbitals. For that reason, they did not have to include the usual $(N+1)$-electron bound terms in their close-coupling expansion, but they did have to include extra potential terms due to

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non-zero overlaps between the continuum orbitals and the bound orbitals, as well as overlap terms between the 3d and 3d′ orbitals. They found a large effect due to term dependence, but like Burke *et al* (1983), they still obtained a large resonant feature that was not observed in the experiment.

In the present work, we make use of the *R*-matrix method (see Burke and Robb 1975) as coded for the Opacity Project (see Berrington *et al* 1987) to carry out a number of close-coupling calculations for the inner-shell excitation of Ca^+. We first discuss the basis set used to generate our bound-state orbitals. Term dependence in the $3p^5 3d(^1P)4s\ ^2P$ term can be simulated with a single 3d orbital by including configuration interaction (CI) along the Rydberg series between the $3p^5 3d4s$ configuration and the $3p^5 nd4s$ configurations with $n \geq 4$ (see, for example, Griffin and Pindzola 1983). The mixing with these higher Rydberg states is large for the $3p^5 3d(^1P)4s\ ^2P$ term where term dependence is significant and quite small for the other terms, where it is not important. Our orbitals were generated by solving for them in an *nl*-dependent model potential generated from Slater-type orbitals according to the prescription of Burgess (see Burgess *et al* 1989) and incorporated into the SUPERSTRUCTURE code (Eissner *et al* 1974) by one of us (NRB). With these particular orbitals, the mixing between $3p^5 3d(^1P)4s\ ^2P$ and $3p^5 nd(^1P)4s\ ^2P$ terms was found to be very small for $n > 4$, and therefore, we only included the $3p^5 4d4s$ configuration. The configurations $3p^6 4s$ and $3p^6 3d$ were included in our even-parity target expansion and the configurations $3p^6 4p$, $3p^5 3d4s$, $3p^5 4s^2$ and $3p^5 4d4s$ constituted our odd-parity target expansion. We then obtain a $3p^5 3d(^1P)4s\ ^2P$ energy of 34.4 eV compared with 33.6 eV reported by Griffin *et al* (1984), with a HF term-dependent 3d orbital; 37.4 eV by Griffin *et al* (1984), with a configuration-average HF 3d orbital; and 39.2 eV by Burke *et al* (1983), with their form of a configuration-average 3d orbital. We also obtain an oscillator strength of 3.28 for the $3p^6 4s\ ^2S \rightarrow 3p^5 3d(^1P)4s\ ^2P$ excitation compared with the term-dependent result of Griffin *et al* (1984) of 2.73, their configuration-average result was 6.74. When we add the configurations $3p^5 4s4p$ and $3p^5 3d4p$ to our even-parity target expansion and the configuration $3p^5 4p^2$ to our odd-parity target expansion, we obtain an oscillator strength of 2.66. However, we found that this additional configuration mixing had little effect on our excitation cross sections.

In order to investigate the sensitivity of the calculation to the choice of target orbitals, we also carried out calculations with HF orbitals. In this case, the 3d term dependence was introduced by employing a $3p^5 \overline{4d}4s$ configuration, where the $\overline{4d}$ pseudo-orbital was taken to be a suitably normalized linear combination of spectroscopic *n*d orbitals whose coefficients were the configuration mixing coefficients for $3p^5 3d(^1P)4s\ ^2P + 3p^5 nd(^1P)4s\ ^2P$ with $n = 4, 5, 6$. We found that this set of orbitals gave us excitation cross sections that differed very little from those generated using Slater-type orbital model potentials.

We first carried out a 13-state close-coupling calculation ($3p^6 4s$, $3p^6 3d$, $3p^6 4p$, $3p^5 4s^2$ and $3p^5 3d4s$) using the largest (68-state) CI target expansion discussed above. We multiplied each excitation cross section by the appropriate Auger yield, as determined by Griffin *et al* (1984), summed them, and added the result to a direct ionization cross section determined from a single parameter Lotz formula (Lotz 1969), scaled to agree with experiment at the lower energies. We compare the results of this calculation, convoluted with a 0.2 eV FWHM Gaussian, with the experiment by Peart *et al* (1989) in figure 1. We see that there is no evidence of a large dielectronic capture resonance, and our results are in much better agreement with experiment, although still somewhat high.

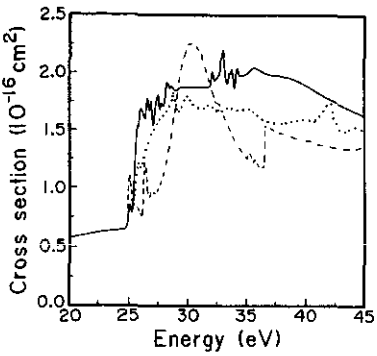

Figure 1. Electron impact ionization cross sections for Ca^+. ——, 13-state close-coupling calculation; – – –, 4-state close-coupling calculation; both from this work, convoluted with a 0.2 eV FWHM Gaussian, and added to a direct ionization cross section determined from the Lotz formula, scaled to experiment; · · · ·, experiment due to Peart *et al* (1989).

To shed light on the earlier theoretical problems, we also carried out a calculation retaining only the three terms of $3p^5 3d4s$ that were used in the previous close-coupling calculations, and without term dependence. The result, multiplied by the Auger yield and added to our estimate of the direct ionization cross section, is also shown in figure 1. It is similar to the results obtained by Burke *et al* (1983) and Pindzola *et al* (1987). If we add the $3p^5 4d4s$ configuration to the target expansion and carry out the same close-coupling calculation, the large resonance just shifts to a higher energy.

There are two possible problems associated with the calculations which include only a few terms from the $3p^5 3d4s$ configuration. First of all, when the continuum orbitals are forced to be orthogonal to bound orbitals with the same angular symmetry, as in the case of the calculation of Burke *et al* (1983) and the present calculation, one must explicitly include $(N+1)$-electron bound-state terms, associated with configurations such as $3p^5 3d4s^2$ and $3p^5 3d^2 4s$, in the close-coupling expansion. However, these $(N+1)$-electron configurations arise not only from the three terms of the $3p^5 3d4s$ configuration included in the close-coupling expansion but also from those six terms that are not included. In the case of a configuration such as $3p^5 3d4s^2$, it is possible to eliminate the terms not arising from the $3p^5 3d(^{1,3}P)$ parents; however, for $3p^5 3d^2 4s$ this is not possible. Thus we have an imbalance between the N-electron bound states and the $(N+1)$-electron bound states within the close-coupling expansion. A similar problem for the case of Fe^+ has been discussed by Berrington *et al* (1988).

A second problem arises from the fact that, when only a few N-electron terms arising from a given configuration are included in the continuum-state expansion, a given dielectronic capture resonance has a correspondingly limited number of possible Auger channels. However, when all the possible terms of this configuration are included, the collision strength of the resonance is redistributed over more Auger channels with interference between each. Thus, the inclusion of additional N-electron terms in the close-coupling expansion will increase the size of the direct excitation cross section, but will tend to decrease the size of the resonance structures. It is interesting to note that in the calculation of Pindzola *et al* (1987), the problem with imbalance discussed above does not exist, since the $(N+1)$-electron states were not included explicitly in the close-coupling expansion. Thus, any resonances in this calculation are due only

to bound channels arising from the N-electron terms included in the expansion. The fact that the large resonance feature still appears in this calculation may indicate that the most serious problem with all these earlier close-coupling calculations is the limited number of Auger channels.

It is important to remember that dielectronic capture resonances will only contribute to the ionization cross section if they Auger to an autoionizing state of the N-electron ion which then autoionizes to a state of the $(N-1)$-electron ion. However, in addition to radiative decay to a bound state of the $(N+1)$-electron ion, they can also autoionize to a bound state of the N-electron ion and not contribute to the ionization cross section. For ions in low stages of ionization, the rate of autoionization will, for most resonant states, be much faster than radiative decay. However, the possibility of Auger emission to bound states must be included in the calculation. This can be done in the close-coupling approximation, in theory, by including a sufficient number of singly excited N-electron bound states in the close-coupling expansion. In our calculations, we only included the $3p^64s$, $3p^63d$, and $3p^64p$ singly excited states. However, the perturbation theory calculations of Auger rates shown in table 1 of Pindzola *et al* (1987) would indicate that, in the case of Ca^+, the doubly-excited state terms are much more strongly coupled to each other than to the singly excited states, and the omission of additional singly excited states should have a small effect on the results. We tested this by performing an 11-state R-matrix close-coupling calculation in which the $3p^63d$ and $3p^64p$ states were excluded and found the effect on the overall cross section to be small. However, the effects on the capture resonances themselves may be large, but look small when viewed against a large excitation–autoionization background. In other cases, the inclusion of a sufficient number of singly excited states will be quite important for an accurate determination of the contribution of dielectronic capture resonances to the ionization cross section (see Tayal and Henry 1990).

It is also possible to calculate the contribution of dielectronic capture resonances to ionization cross sections using the independent processes approximation, in which the resonance contribution is represented as the cross section for dielectronic capture times a branching ratio for sequential Auger emission of two electrons. This is especially advantageous for highly ionized species where the effects of continuum coupling are much smaller; the number of states which must be included in the calculation is much larger, since it is determined by the number of intermediate-coupled levels rather than the number of LS terms; and radiative branching is very important (see Chen *et al* 1990).

In addition to the autoionizing configurations $3p^53d4s$ and $3p^54s^2$, one should also include the $3p^53d^2$ configuration in the close-coupling expansion. It can contribute only through bound-state configuration interaction and continuum coupling, since it cannot be excited directly from the $3p^64s$ ground state. However, since it is in the same energy region as the two doubly excited configurations included in the calculation and it mixes strongly with $3p^53d4s$, it could have an effect on the results. Therefore, we also performed a 32-state calculation in which the 19 terms from $3p^53d^2$ were added to the close-coupling expansion; this results in an 87-state CI target expansion. The results are very similar to those shown in figure 1. Apparently there is some transfer of collision strength from $3p^53d4s$ to $3p^53d^2$, but interference effects between terms of these two configurations seem to be small. Finally, contributions from excitation to higher-energy autoionizing terms, especially the $3p^54s4d$ configuration, are to be expected above about 35 eV, as are resonances attached to them. These higher energy configurations would be required to explain, for example, the experimental feature at about 42 eV.

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