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LETTER TO THE EDITOR

Convergence of the close-coupling method for the $3p^53d^2$ configuration in Ti^{3+}

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Abstract. By performing 21-state and 26-state *R*-matrix calculations for Ti^{3+}, we have explored the convergence of the close-coupling approximation for electron-impact excitation from the $3p^63d$ ground state to the $3p^53d^2$ doubly-excited states. Both calculations included all 19 terms of the $3p^53d^2$ configuration and they differed only in the number of singly-excited states included. Three terms of $3p^53d^2$ are autoionizing and their excitation-autoionization contributions dominate the ionization cross section in the threshold region. Our results from either the 21-state or 26-state calculations for excitation to these three terms, when combined with the background direct cross section, are in excellent agreement with crossed-beam measurements of the ionization cross section and improved over earlier 10-state *R*-matrix calculations. This illustrates the importance of including coupling between all terms within a doubly-excited configuration, as shown earlier in the case of Ca^+ by Badnell *et al.* Furthermore, the 26-state calculation shows a strong reduction in the resonance structure associated with excitation to the 16 bound terms of $3p^53d^2$, as compared to the 21-state calculation; this clearly illustrates the importance of including a sufficient number of singly-excited states in a close-coupling calculation of inner-shell excitation. Finally the 26-state calculation has also enabled us to determine valence-shell excitation cross sections from the $3p^63d$ ground state to $3p^64s$ and $3p^64p$ and from the $3p^64s$ metastable state to $3p^64p$.

It was first demonstrated experimentally by Falk *et al* (1981, 1983) that inner-shell excitations of the form $np^6nd \rightarrow np^5nd^2$, followed by autoionization, enhance the ionization cross sections of Ti^{3+}, Zr^{3+} and Hf^{3+} by more than an order of magnitude in the threshold region. Ti^{3+} is a particularly interesting case since only three of the 19 terms of the $3p^53d^2$ are autoionizing; however, the transitions from the $3p^63d$ ground state to these three terms are dipole allowed, and the cross section is large enough to dominate the ionization cross section, even though the branching ratio for autoionization from one of these terms is relatively small (Griffin *et al* 1982). Distorted-wave calculations of the $3p^63d \rightarrow 3p^53d^2$ transition were performed by Bottcher *et al* (1983); however, their calculated results were nearly a factor of two higher than experiment. Burke *et al* (1984) performed a *R*-matrix calculation of this transition in which they included nine terms of $3p^53d^2$ in their close-coupling expansion and obtained results which where improved over the distorted-wave calculations, but still approximately 50% higher than the measurement in the threshold region.

In the present work, we have employed the *R*-matrix method as coded for the Opacity Project (see Berrington *et al* 1987) to carry out close-coupling calculations of inner-shell and valence-shell excitation cross sections for this ion. The bound-state orbitals were generated from a single-configuration Hartree–Fock calculation and then used to construct a configuration-interaction (CI) basis set. In our first calculations, we included only the 3p^{6}3d and 3p^{6}4s singly-excited states and the 19 terms from 3p^{5}3d^2 in a 21-state close-coupling expansion. However this calculation resulted in very large resonances associated with excitation to the 16 bound terms of the 3p^{5}3d^2 configuration. Therefore, we investigated the effects of coupling with singly-excited states on these resonant structures by performing a 26-state calculation which included 3p^{6}3d, 3p^{6}4s, 3p^{6}4p, 3p^{6}4d, 3p^{6}5s, 3p^{6}5p, 3p^{6}4f and all 19 terms of 3p^{5}3d^2. This also enabled us to make calculations of valence shell excitation cross sections from the ground state to 3p^{6}4s and 3p^{6}4p as well as from the 3p^{6}4s metastable state to 3p^{6}4p.

The energies obtained from a calculation which included all 26 terms mentioned above in the CI basis set are shown in column two of table 1. The calculated energies for the singly-excited states can be compared with the experimental energies (Wiese and Musgrove 1989) shown in column three of this table. In our earlier work on Ti^{3+} (Griffin *et al* 1982), it was found that one could obtain good agreement with experimental energies for the bound states of 3p^{5}3d^2 in the isoelectronic ion V^{4+} by scaling

Table 1. Energies for the singly-excited terms and the terms of the 3p^{5}3d^2 configuration included in the 26-state calculation for Ti^{3+}. The designations for the 3p^{5}3d^2 terms include the principal eigenvector components of the various 3d^2 parent terms which are coupled to 3p^5 ^{2}P to form the total *LS*. The experimental energies are from Wiese and Musgrove (1989).

	Energies (eV)		
LS term designations	CI basis	Experimental	Scaled Slater parameters
3p^{6}3d ^{2}D	0.00	0.00	
3p^{6}4s ^{2}S	10.64	9.94	
3p^{6}4p ^{2}P	16.39	15.90	
3p^{6}4d ^{2}D	24.75	24.38	
3p^{6}5s ^{2}S	26.63	26.31	
3p^{6}5p ^{2}P	28.85	28.59	
3p^{6}4f ^{2}F	29.46	29.25	
3p^{5}3d^2:			
$0.864(^3\mathrm{F})+0.503(^3\mathrm{P})\,^4\mathrm{D}$	31.08		32.48
$1.000(^3\mathrm{F})\,^4\mathrm{G}$	33.04		34.06
$1.000(^3\mathrm{P})\,^4\mathrm{P}$	33.16		34.15
$1.000(^3\mathrm{F})\,^4\mathrm{F}$	34.22		35.01
$0.886(^1\mathrm{D})-0.458(^3\mathrm{F})+0.075(^3\mathrm{P})\,^2\mathrm{D}$	34.49		35.22
$-0.715(^1\mathrm{G})+0.686(^3\mathrm{F})-0.126(^1\mathrm{D})\,^2\mathrm{F}$	34.70		35.37
$-0.812(^1\mathrm{D})+0.485(^3\mathrm{P})-0.324(^1\mathrm{S})\,^2\mathrm{P}$	35.41		35.95
$1.000(^1\mathrm{G})\,^2\mathrm{H}$	36.06		36.48
$0.953(^3\mathrm{F})+0.302(^1\mathrm{G})\,^2\mathrm{G}$	36.35		36.72
$0.990(^1\mathrm{D})+0.102(^3\mathrm{F})-0.081(^1\mathrm{G})\,^2\mathrm{F}$	36.44		36.78
$0.864(^3\mathrm{P})-0.503(^3\mathrm{F})\,^4\mathrm{D}$	37.18		37.39
$-0.939(^3\mathrm{P})+0.266(^3\mathrm{F})+0.217(^1\mathrm{D})\,^2\mathrm{D}$	38.98		38.83
$1.000(^3\mathrm{P})\,^4\mathrm{S}$	39.36		39.14
$1.000(^3\mathrm{P})\,^2\mathrm{S}$	39.36		39.14
$0.953(^1\mathrm{G})-0.302(^3\mathrm{F})\,^2\mathrm{G}$	39.58		39.32
$0.895(^1\mathrm{S})-0.429(^1\mathrm{D})-0.119(^3\mathrm{P})\,^2\mathrm{P}$	41.67		41.00
$-0.720(^3\mathrm{F})-0.690(^1\mathrm{G})+0.021(^1\mathrm{D})\,^2\mathrm{F}$	46.20		44.57
$-0.866(^3\mathrm{P})-0.395(^1\mathrm{D})-0.305(^1\mathrm{S})\,^2\mathrm{P}$	50.47		48.06
$-0.848(^3\mathrm{F})-0.410(^1\mathrm{D})-0.335(^3\mathrm{P})\,^2\mathrm{D}$	51.80		49.14

the electrostatic Slater parameters by a factor of 0.80 to correct for correlation effects. This same scaling factor was employed for Ti^{3+} and led to improved agreement with the thresholds for excitation autoionization in the experimental ionization cross section. The energies obtained for the terms of $3p^53d^2$ by employing scaled Slater parameters are shown in the fourth column of table 1. In the present scattering calculations, the excited-state thresholds were adjusted to the experimental energies for the singly-excited states and to the energies obtained by using scaled Slater parameters for $3p^53d^2$. With the *R*-matrix programs, such energy adjustment can be performed in a way to obtain consistency between the inner and outer regions by making a corresponding adjustment in the diagonal elements of the inner-region Hamiltonian matrix before diagonalization (Berrington 1985).

We first consider ionization of Ti^{3+}. The direct ionization cross section from the 3d subshell, with an experimental ionization energy of 43.27 eV (Wiese and Musgrove 1989), was determined using our configuration-average distorted-wave ionization program (Griffin *et al* 1987). The results are in close agreement with those obtained from the Lotz formula (Lotz 1968, 1969) used in previous work on the ionization of Ti^{3+}. The excitation cross sections to the three autoionizing terms of the $3p^53d^2$ configuration, obtained from the 26-state *R*-matrix calculation, were then multiplied by the branching ratios for autoionization and added to the direct ionization cross section. We employed branching ratios of 1.00 for the ^2F term, 0.996 for the ^2P term and 0.416 for the ^2D term, as determined in earlier calculations on this ion (Griffin *et al* 1982). Finally the total ionization cross section was convoluted with a 2.0 eV Gaussian distribution to simulate the experimental electron-energy distribution.

The results of this calculation in comparison with the measurements of Falk *et al* (1981, 1983) are shown in figure 1. They are seen to be in excellent agreement with experiment. By comparing this theoretical cross section with that obtained from the earlier distorted-wave calculations (Bottcher *et al* 1983), it is obvious that continuum

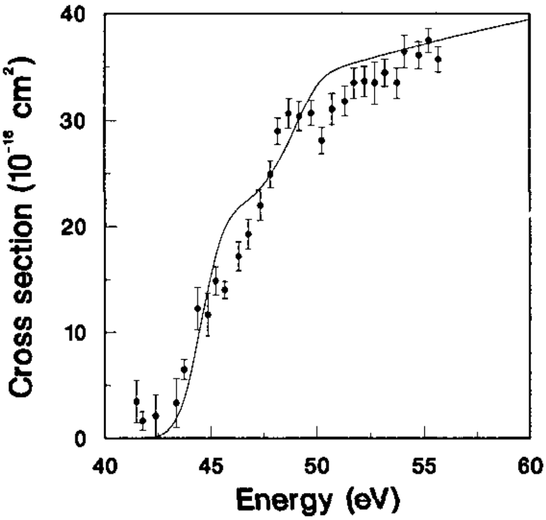

Figure 1. Electron-impact ionization cross section for Ti^{3+}. Full curve, 26-state calculation of excitation to the three autoionizing terms of $3p^53d^2$, multiplied by the autoionizing branching ratios, added to a distorted-wave calculation of the direct ionization cross section, and convoluted with a 2.0 eV Gaussian. Full circles, experimental measurements of Falk *et al* (1981, 1983).

coupling between these three terms and the lower terms of $3p^5 3d^2$ is very important. The *R*-matrix calculation of Burke *et al* (1984) included only the nine terms of $3p^5 3d^2$ that can be reached from the ground state by dipole-allowed transitions; namely, the three autoionizing terms plus the bound ^2P, ^2D and ^2F terms. The fact that their calculated cross section is still about 50% higher than experiment would indicate that coupling with the other bound terms is also quite important. It was found earlier (Badnell *et al* 1991a) that coupling between the various terms of the autoionizing configuration $3p^5 3d4s$ in Ca^+ has a pronounced effect on the resonance structure associated with this configuration, and that all terms must be included in the close-coupling expansion in order to obtain reasonable agreement with experiment. In the present case, it is also important to include all the terms of $3p^5 3d^2$ in the close-coupling expansion; however, here the effect is primarily on the background excitation cross section rather than the resonance structure. Finally it is worth noting that the result obtained from our 21-state *R*-matrix calculation is almost identical to that obtained from the 26-state calculation; thus, coupling with the singly-excited states has a very small effect on the cross section to the three highest terms of $3p^5 3d^2$.

We now consider the excitation cross section to the 16 bound terms of $3p^5 3d^2$. The result of our 26-state calculation for the total cross section to these terms is shown in figure 2(*a*). The background cross section is about a factor of two lower than the earlier distorted-wave results (Bottcher *et al* 1983). However, the cross section is enhanced by a pronounced resonance structure due to dielectronic capture into $3p^5 3d^2 nl$ resonant states followed by autoionization to the lower terms of $3p^5 3d^2$. However, the results of our earlier 21-state calculation, which is shown in figure 2(*b*), shows a much stronger resonance structure. By including the additional singly-excited $3p^6 4p$, $3p^6 4d$, $3p^6 5s$, $3p^6 5p$ and $3p^6 4f$ terms in the close-coupling expansion for the 26-state calculation, more autoionizing channels exist for the $3p^5 3d^2 nl$ resonant states and this significantly reduces the size of the resonance structure associated with excitation to $3p^5 3d^2$. By examining the resonant contributions to the cross sections for excitation to the various $3p^6 nl$ terms in the energy range above the highest singly excited-state

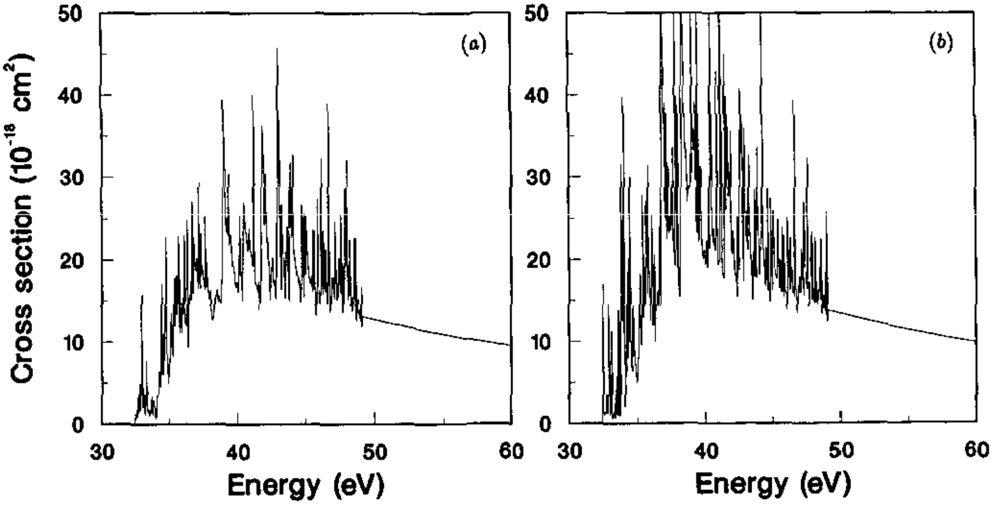

Figure 2. *R*-matrix calculation of the excitation cross section to the 16 bound terms of $3p^5 3d^2$ of Ti^{3+}. Results of 26-state calculation are shown in (*a*); results of 21-state calculation are shown in (*b*).

threshold, we conclude that autoionization from the $3p^53d^2nl$ resonances to the singly-excited $3p^64f$ term is especially significant; however, autoionization to the $3p^64d$, $3p^65s$ and $3p^65p$ terms is also too important to ignore. Thus, even the 26-state calculation is not sufficiently complete to insure an accurate cross section for excitation to the bound terms of $3p^53d^2$; the addition of more singly-excited terms to the close-coupling expansion would further reduce the resonant contribution.

This case then clearly illustrates a general difficulty in obtaining convergence of the close-coupling expansion for excitation to doubly-excited states, be they bound or autoionizing. If the resonant states attached to high lying doubly-excited states are strongly coupled to the adjacent continuua associated with the singly-excited states as well as the lower lying doubly-excited states, it is very difficult to include a sufficient

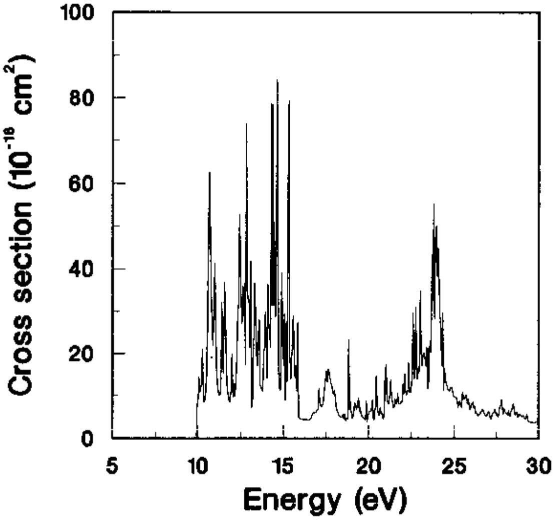

Figure 3. 26-state *R*-matrix calculation of the $3p^63d \rightarrow 3p^64s$ excitation in Ti^{3+}.

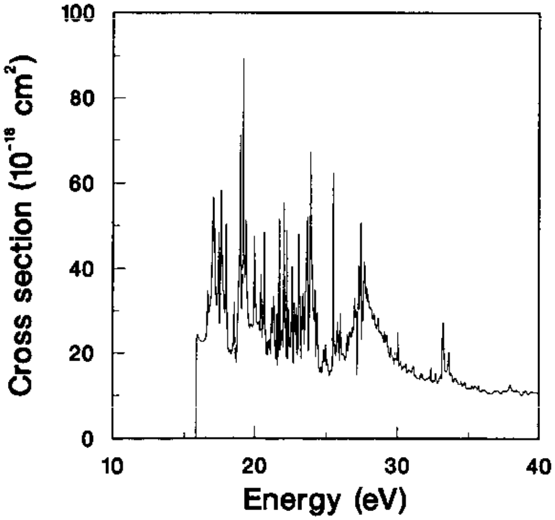

Figure 4. 26-state *R*-matrix calculation of the $3p^63d \rightarrow 3p^64p$ excitation in Ti^{3+}.

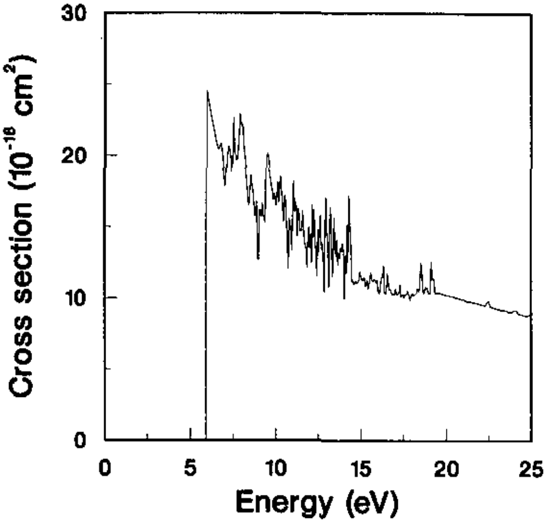

Figure 5. 26-state *R*-matrix calculation of the $3p^64s \rightarrow 3p^64p$ excitation in Ti^{3+}.

number of singly-excited states in the close-coupling calculation to determine the magnitude of the resonance structure associated with the lower lying doubly-excited states accurately. This problem always exists in calculating the contribution of dielectronic capture resonances to the ionization cross section of a given ion. In order to contribute to ionization, the resonant states must autoionize to an autoionizing level which can then emit a second Auger electron. However, they can also autoionize to bound states, which must be included in the close-coupling expansion or the resonance contribution will be overestimated (see Tayal and Henry 1990).

Such resonance contributions to excitation (see Badnell *et al* 1991b) or ionization (see Chen *et al* 1990) can also be calculated using the independent-processes approximation, in which the cross section for dielectronic capture is multiplied by a branching ratio for autoionization to a particular excited level, in the case of excitation, or the branching ratio for sequential Auger emission of two electrons, in the case of ionization. This approximation, which is especially appropriate for higher stages of ionization where continuum coupling effects are much smaller and the effects of radiative branching and relativistic effects are much larger, allows for the inclusion of a large number of possible Auger channels. However, cases such as the $3p^53d^2$ configuration in Ti^{3+} are particularly difficult; continuum coupling effects are too strong to expect accurate results from the independent-processes approximation and important autoionization transitions from dielectronic capture resonances to a large number of lower lying singly-excited states makes it difficult to obtain convergence of the close-coupling approximation.

Finally we consider the excitation cross sections associated with valence-shell transitions. In an earlier paper, distorted-wave and three-state close-coupling calculations of the $3p^63d \rightarrow 3p^64s$, $3p^63d \rightarrow 3p^64p$ and $3p^64s \rightarrow 3p^64p$ transitions in Ca^+, Sc^{2+}, Ti^{3+}, Cr^{5+} and Fe^{7+} were compared (Pindzola *et al* 1989). This work was only intended to study coupling effects as a function of ionization stage; three-state calculations are not sufficiently complete to generate accurate cross sections and do not include important resonant contributions. However, the present 26-state calculation has enabled us to determine accurate cross sections for these transitions in Ti^{3+} including the effects of dielectronic capture resonances. Our results for the excitation cross sections from the ground state to the $3p^6 4s$ and $3p^6 4p$ terms are shown in figures 3 and 4, respectively. As can be seen, the resonance enhancement of the cross sections is strong for both the $3d \rightarrow 4s$ and $3d \rightarrow 4p$ transitions and would have a significant effect on the excitation rate coefficient for this ion. The cross section for excitation from the $3p^6 4s$ metastable term to the $3p^6 4p$ term is shown in figure 5. The background cross section is quite large and, as one would expect, the relative contribution of the resonances is much smaller than for the much weaker $3d \rightarrow 4s$ dipole forbidden transition.

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