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Configuration-interaction effects on the electron-impact ionization of Ti^{3+}

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Abstract. Using a recently developed, unified version of both *R*-matrix and distorted-wave methods, we have carried out new calculations for the electron-impact ionization of Ti^{3+} and found that the previous calculations of Griffin *et al* are incorrect. Contrary to one of the major conclusions of that paper, coupling between the three autoionizing and the sixteen bound *LS* terms of the $3p^53d^2$ configuration is not important. However, the other major conclusion of that paper that the inclusion of singly-excited states is necessary to provide an alternate decay path for resonances remains valid. Further calculations including configuration-interaction (CI) mixing with correlation configurations formed by the double-electron promotions $3p^2 \rightarrow 3d^2$ were necessary to achieve reasonable agreement with experiment. A larger close-coupling calculation which included $3p^64s$ and $3p^53d4s$ target states and the corresponding $3p^2 \rightarrow 3d^2$ correlation configurations provided further improvements in the results. Potential problems with pseudo-resonances are found to be effectively diagnosed by comparison of distorted-wave and *R*-matrix results.

1. Introduction

Joint theoretical and experimental results for the electron-impact ionization of Ti^{3+} (Falk *et al* 1981) first showed that a large enhancement in the threshold cross section was due to $3p^63d \rightarrow 3p^53d^2$ excitation–autoionization. Since that time, a number of calculations have confirmed this, although the disagreement between theory and experiment has never been fully resolved. Theoretical calculations consistently resulted in a threshold-region cross section much larger than the experimental value of ~30 Mb at 50 eV. First, a Coulomb–Bethe method (Griffin *et al* 1982) led to a cross section of ~80 Mb at 50 eV. Next the full distorted-wave calculations of Bottcher *et al* (1983) and Pindzola *et al* (1985) resulted in a value of ~60 Mb at this energy. Then Burke *et al* (1984) performed a 10-state *R*-matrix calculation which resulted in a cross section of ~ 50 Mb at 50 eV, still much larger than the experimental value of ~ 30 Mb. In an attempt to explain this discrepancy, Griffin *et al* (1991) (hereafter referred to as I) performed 21-state and 26-state *R*-matrix calculations for this transition, and found that their results were in good agreement with experiment. This seemed to indicate that coupling effects were strong between the highest three autoionizing *LS* terms of the $3p^53d^2$ configuration and the 16 bound terms.

Recently we have developed a unified version of distorted-wave and *R*-matrix methods, using identical angular algebra and target orbitals, in order to study channel-coupling effects in the excitation–autoionization of krypton ions (Gorczyca *et al* 1993). As a test of the importance of coupling effects, we reinvestigated the excitation–autoionization of Ti^{3+} using both methods. During this study, it was discovered that certain $LS\Pi$ symmetries had inadvertently been omitted in the previous R-matrix calculations of I, so that a re-examination of this calculation is warranted. Our approach will be to first correct the previous results by including the symmetries which were omitted. Then coupling effects will be studied by comparing R-matrix and distorted-wave results. Finally, improvements to this single-configuration calculation will be investigated by allowing configuration-interaction (CI) mixing in the target atomic states.

2. Single-configuration results

In the present study, we use the R-matrix version which was coded for the Opacity Project (see Berrington *et al* 1987). The target basis is described in I, and the atomic orbitals were generated with the MCHF structure package of Froese Fischer (1991). We repeated the earlier 26-state calculations including 42 $LS\Pi$ symmetries of the form $S = \{1, 3\}$, $L = \{0, \ldots, 10\}$, and $\Pi = \pm 1$, except for $L = 0$, where $\Pi = +1$ only. In I, terms up to $L = 15$ were included, but the parities $\Pi = (-1)^{L+1}, L > 0$ were mistakenly omitted. This is not a problem for excitation into or out of the $3p^64s$ state, since these parities are not allowed. However, when both the initial and final states have angular momentum greater than zero, these parities must be included. As a consistency check, we calculated the $3p^63d \rightarrow 3p^64s$ and $3p^64s \rightarrow 3p^64p$ excitation cross sections with all 42 $LS\Pi$ symmetries and duplicated the results given in figures 3 and 5 of I. The $3p^63d \rightarrow 3p^64p$ calculation, on the other hand, requires these symmetries. We show the results for this transition in figure 1, where it is apparent that more resonance structure exists than in the previous calculation, and also that the background cross section is about 50% higher than that of I.

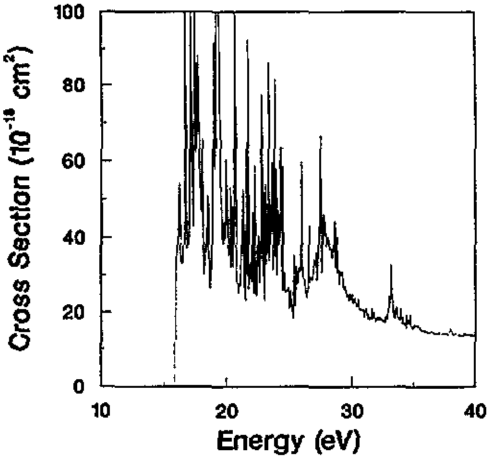

Figure 1. 26-state R-matrix cross section of the $3p^63d \rightarrow 3p^64p$ excitation of Ti^{3+}.

The sum of excitation cross sections to the 16 non-autoionizing states of the $3p^53d^2$ configuration from a 26-state R-matrix calculation is shown in figure 2, where for this case the background cross section is twice as large as that in the previous calculation (figure 2 of I) due to the inclusion of the extra symmetries. One of the key findings of I was that the resonance contribution to the total cross section was reduced in going from a 21-state to a 26-state calculation since the inclusion of additional singly-excited states provided an

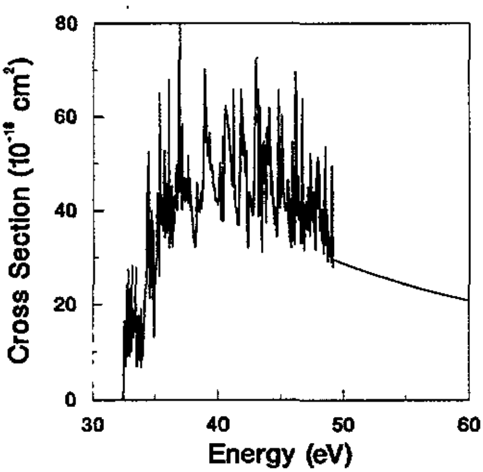

Figure 2. 26-state R-matrix cross section of the excitation to the 16 bound $3p^53d^2$ terms of Ti^{3+}.

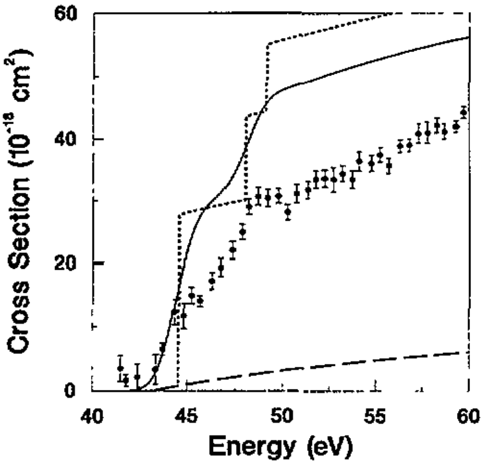

Figure 3. Electron-impact ionization cross section for Ti^{3+}; ——, 26-state calculation of excitation to the three autoionizing terms of $3p^53d^2$, multiplied by the autoionizing branching ratios, added to a distorted-wave calculation of the direct ionization cross section, and convoluted with a 2.0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

alternate decay path for these resonances. This remains valid for the present calculation since this reduction occurs independently within each partial symmetry. Such an effect was also observed in the study of Sc^{2+} (see Pindzola *et al* 1993).

We show the total ionization cross section obtained from this 26-state calculation in figure 3 along with distorted-wave and experimental results. These and all subsequent results were determined by multiplying each excitation cross section by the appropriate branching ratio (Griffin *et al* 1982), and then adding the sum of these to the direct ionization cross section, which was computed using a configuration-average distorted-wave method (Younger 1980). The present LS-coupled distorted-wave results are consistent with the intermediate-coupled distorted-wave results of Pindzola *et al* (1985). The present R-matrix results are about 10% lower than the distorted-wave results, indicating that a small amount of channel coupling exists. The R-matrix results of Burke *et al* (1984) were about 5% lower than the present R-matrix results, which can be attributed solely to the fact that our threshold energies are shifted lower by about 5% as in I, leading to a $1/E$ energy scaling of +5%. These energy shifts were based on a 0.80 scaling of the Slater parameters, which was seen to give improved energy thresholds for the isoelectronic $3p^53d^2$ states in V^{4+}. It is unclear whether this leads to improvements in threshold energies of Ti^{3+}, however, and so while we

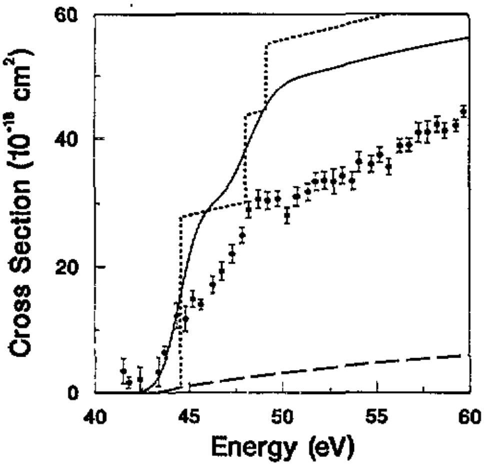

Figure 4. Electron-impact ionization cross section for Ti^{3+}; ——, 4-state, single configuration *R*-matrix calculation, convoluted with a 2.0 eV FWHM Gaussian; - - - -, corresponding distorted-wave calculation, unconvoluted. — — —, direct-ionization contribution; ●, experimental measurements of Falk *et al* (1981, 1983).

use this same energy shift for comparison purposes, we will rely on the *ab initio* theoretical values for the final calculation.

In I it was found that the 21-state and 26-state excitation–autoionization results were almost identical. We compared these two cases and again found almost perfect agreement. It is found that the present 26-state results and the 10-state results of Burke *et al* are quite similar except for the small energy-shifting effect. We also performed a 4-state calculation including just the ground and the three autoionizing states, and show these results in figure 4. The resulting cross section is still nearly identical to the 26-state cross section, indicating that channel-coupling to the six singly-excited $3p^6n\ell$ states and the sixteen non-autoionizing $3p^53d^2$ states is negligible. Thus, it should be possible to study additional CI effects within a much smaller, 4-state calculation including only the ground and three autoionizing states.

3. Configuration-interaction results

In earlier studies of the oscillator strengths from the $3p^63d$ ground state to the $3p^53d^2$ autoionizing states of Ti^{3+} (Griffin *et al* 1982, Hibbert *et al* 1982 and Tiwary *et al* 1983) it was found that CI mixing within the initial and final states reduced the oscillator strengths by about 20–30%. In table 1 we have listed energies and oscillator strengths for single-configuration and multi-configuration target states, where the $3p^43d^3$ and $3p^33d^4$ configurations were mixed with the ground and excited states, respectively. We determined that mixing of the upper three $3p^53d^2$ terms with the $3p^33d^4$ configuration has little effect on the dipole matrix elements but does effect the energies. The single-configuration oscillator strengths to the three uppermost *LS* terms, allowing for mixing of like-symmetry terms within the $3p^53d^2$configuration, are within 1% of the values reported by Burke *et al* (1984) and Tiwary *et al* (1983). By including additional CI mixing, the length form of the oscillator strengths is reduced by 15–25%, and furthermore, the length and velocity forms become more consistent with each other. We note that the CI oscillator strengths reported by Tiwary *et al* (1983) are more accurate, since they used different 3p and 3d orbitals for the initial and final states, thereby allowing for relaxation effects.

The effect of CI mixing on the excitation–autoionization cross section was then investigated by using the target states of table 2 in 4-state *R*-matrix and distorted-wave calculations, with the thresholds adjusted to the same energies used in I. Figure 5 shows

Table 1. Ti^{3+} energies, E (eV), and oscillator strengths, f.

	Single configuration		CI	
	E	f	E	f
$3p^63d(^2D)$	0.00		0.00	
$3p^53d^2[-0.720(^3F) - 0.690(^1G) + 0.021(^1D)]\ (^2F)$	45.48	1.68 L 1.09 V	46.29	1.23 L 1.35 V
$3p^53d^2[-0.866(^3P) - 0.395(^1D) - 0.305(^1S)]\ (^2P)$	50.46	1.12 L 0.58 V	50.72	0.96 L 0.66 V
$3p^53d^2[-0.848(^3F) - 0.410(^1D) - 0.335(^3P)]\ (^2D)$	51.80	2.31 L 1.15 V	51.13	1.71 L 1.50 V

Table 2. Target and $(N + 1)$-electron configurations included in the Ti^{3+} 4-state R-matrix calculations.

Target description	N-electron	$(N + 1)$-electron
single configuration	$3p^63d$ $3p^53d^2$	$3p^63d^2$ $3p^53d^3$
CI	$3p^63d$ $3p^53d^2$ $3p^43d^3$ $3p^33d^4$	$3p^63d^2$ $3p^53d^3$ $3p^43d^4$ [a] $3p^33d^5$ [a]

[a] Omitted from calculation shown in figure 6.

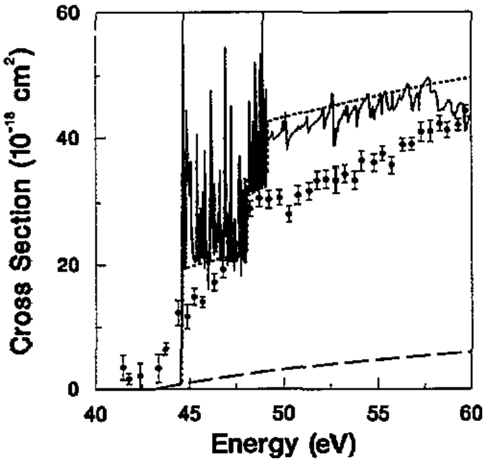

Figure 5. Electron-impact ionization cross section for Ti^{3+}; ——, 4-state R-matrix calculation with CI mixing in the target states; ----, corresponding distorted-wave calculation; — — —, direct-ionization contribution; ●, experimental measurements of Falk *et al* (1981, 1983).

these results, for which we have not convoluted the R-matrix results in order to highlight certain features above the final threshold. We see better overall agreement with experiment, owing primarily to the reduction of the dipole matrix elements mentioned above in the oscillator strength study. But while CI mixing has reduced the cross section for either method, the R-matrix results show prominent resonance structure above final threshold, and furthermore, the gap between the R-matrix and distorted-wave results appears to have narrowed from the 10% difference found in the single-configuration calculations. These features can be identified as pseudo-resonances arising from the inclusion of the $3p^43d^4$

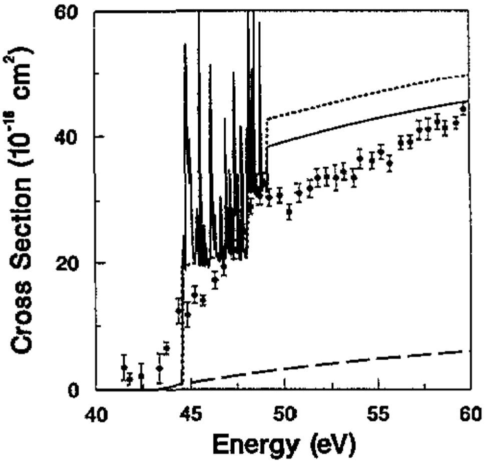

Figure 6. Electron-impact ionization cross section for Ti^{3+}; ——, 4-state *R*-matrix calculation with CI mixing in the target states, omitting correlating $N+1$-electron states (see text); - - - -, corresponding distorted-wave calculation; — — —, direct-ionization contribution; ●, experimental measurements of Falk *et al* (1981, 1983).

and $3p^3 3d^5$ $(N+1)$-electron configurations in the total wavefunction description. This inclusion appears, at first glance, to be necessary in order to compensate for the enforced orthogonality of the continuum orbitals to the 3p and 3d orbitals, since these continuum orbitals are coupled to certain admixtures of the $3p^4 3d^3$ and $3p^3 3d^4$ correlating configurations in the target states. However, the admixture of any one correlating configuration is quite small, so that the full inclusion of these additional $(N+1)$-electron configurations actually overcompensates for the orthogonality procedure. We note that the present distorted-wave calculations use non-orthogonal continuum and bound orbitals, and compensate for this by including energy-dependent exchange-overlap terms in the Hamiltonian. Therefore, additional $(N+1)$-electron configurations do not need to be included, so that pseudo-resonances do not occur for this method.

In a recent study on krypton ions (Gorczyca *et al* 1993), the inclusion of similar correlating $(N+1)$-electron configurations yielded physically unmeaningful results. It was also found that those $(N+1)$-electron configurations responsible for the pseudo-resonances could not be omitted without also removing a significant contribution to the continuum-orbital description. That was because the corresponding correlating N-electron configurations corrected for large relaxation and term-dependent effects, and therefore mixed strongly with the target states. In the present case, however, CI mixing between the correlating N-electron configurations $3p^4 3d^3$ and $3p^3 3d^4$ and the $3p^6 3d$ and $3p^5 3d^2$ target-state configurations is so small that the corresponding $(N+1)$-electron configurations $3p^4 3d^4$ and $3p^3 3d^5$ contribute insignificantly to the continuum-orbital description. Removing these states therefore seems reasonable in order to eliminate the pseudo-resonances. We utilized this removal approximation by performing a 4-state *R*-matrix calculation excluding the $3p^4 3d^4$ and $3p^3 3d^5$ $(N+1)$-electron configurations, and the unconvoluted cross section shown in figure 6 is now smooth above final threshold; furthermore, there remains a constant ~10% difference between *R*-matrix and distorted-wave CI results, similar to that found for the single-configuration case (figure 4). This illustrates the utility of running parallel distorted-wave and *R*-matrix calculations for diagnosing pseudo-resonances.

CI mixing within the ground and three autoionizing target states is seen to give more converged oscillator strengths, and excitation cross sections in better agreement with experiment. However, we found that CI mixing had little effect on oscillator strengths or collision strengths to the lower six $3p^5 3d^2$ ^2F, ^2P, and ^2D terms. We also investigated the effect that CI mixing in the target states might have on the channel coupling of the three autoionizing states to the sixteen bound ones in the following manner. We first performed a 4-state *R*-matrix calculation including the $3p^63d(^2D)$ ground state and all three $3p^53d^2(^2F)$ states, and then a 2-state calculation omitting the two lowest (^2F) states. The excitation cross section to the upper (^2F) state was found to be the same in either case, indicating that channel coupling between autoionizing and bound terms is still negligible for this symmetry, even with CI mixing included.

The upper-three $3p^53d^2$ *LS* terms of Ti^{3+} are thus peculiar in that they are the only three of the nineteen which: (i) couple strongly to the ground state via the dipole operator; (ii) require CI mixing in order to converge oscillator strengths and collision strengths; and (iii) contribute to autoionization. The above considerations also shed light on why single-configuration *R*-matrix calculations yielded results in good agreement with experiment in the case of Sc^{2+} (Pindzola *et al* 1993). For that case, all nineteen terms contribute to autoionization, so that the inaccuracy in the excitation cross section to the upper-three terms leads to a much smaller relative inaccuracy in the total cross section to all nineteen terms.

As a final investigation of channel-coupling and CI effects, we included the target states closest to both the $3p^63d$ ground state and the three $3p^53d^2$ autoionizing states, namely the $3p^64s$ state and the nine $3p^53d4s$ autoionizing states, leading to a 14-state *R*-matrix calculation. Listed in table 3 are the *N*-electron configurations included in the target description. Note that all $3p^2 \rightarrow 3d^2$ promotions are included for CI mixing purposes even though these are not explicitly used as target states in the close-coupling expansion. Also, we only keep $(N+1)$-electron configurations which can be constructed by adding *a bound orbital to an N-electron configuration explicitly included in the close-coupling* expansion, thus avoiding occurrences of pseudo-resonances. This is in accord with the above conclusion that omitting these highly-excited $(N+1)$-electron configurations is valid. In table 4 we list the CI energies of the target states, which are not shifted in the *R*-matrix calculation. Also listed are the branching ratios. These were determined using this larger CI *expansion, and note in particular that the present branching ratio of 0.329 from the highest* ^2D state is considerably lower than the value of 0.416 calculated in I. The results for this 14-state *R*-matrix calculation, which are convoluted with a 2.0 eV FWHM Gaussian to simulate the experimental beam width, are shown in figure 7, and we see adequate agreement with the experimental data in the above-threshold region. The onset for ionization is seen to occur at a lower energy experimentally, however, which indicates that an even larger CI calculation is necessary in order to obtain better threshold energies.

Table 3. Target and $(N+1)$-electron configurations included in the Ti^{3+} 14-state *R*-matrix calculations.

N-electron	$(N+1)$-electron
$3p^63d$	$3p^63d^2$
$3p^64s$	$3p^63d4s$
$3p^53d^2$	$3p^64s^2$
$3p^53d4s$	$3p^53d^3$
$3p^43d^3$	$3p^53d^24s$
$3p^43d^24s$	$3p^53d4s^2$
$3p^33d^4$	
$3p^33d^34s$	

Table 4. CI mixing coefficients, symmetries, Σ, threshold energies, E (eV), and branching ratios, B, for the 14-state R-matrix calculations.

CI coefficients[a]	Σ	E	B
0.986 $3p^63d$	^2D	0.00	
0.984 $3p^64s$	^2S	10.10	
0.991 $3p^53d(^3P)4s$	^4P	45.44	0.999
0.982 $3p^53d(^3P)4s$	^2P	46.37	1.000
0.688 $3p^5[3d^2(^3F)]$ 0.643 $3p^5[3d^2(^1G)]$ −0.279 $3p^53d(^3F)4s$	^2F	46.13	0.999
−0.990 $3p^53d(^3F)4s$	^4F	46.69	0.907
−0.950 $3p^53d(^3F)4s$ −0.200 $3p^5[3d^2(^3F)]$ −0.187 $3p^5[3d^2(^1G)]$	^2F	47.84	1.000
0.991 $3p^53d(^3D)4s$	^4D	49.58	0.947
0.831 $3p^53d(^1D)4s$ 0.363 $3p^5[3d^2(^3F)]$ 0.329 $3p^53d(^3D)4s$ 0.169 $3p^5[3d^2(^1D)]$ 0.138 $3p^5[3d^2(^3P)]$	^2D	49.73	0.854
−0.987 $3p^53d(^1F)4s$	^2F	50.18	0.935
−0.719 $3p^53d(^3D)4s$ 0.514 $3p^53d(^1D)4s$ −0.378 $3p^5[3d^2(^3F)]$ −0.178 $3p^5[3d^2(^1D)]$ −0.143 $3p^5[3d^2(^3P)]$	^2D	50.16	0.996
−0.845 $3p^5[3d^2(^3P)]$ −0.398 $3p^5[3d^2(^1D)]$ −0.283 $3p^5[3d^2(^1S)]$ −0.132 $3p^53d(^3P)4s$	^2P	50.79	0.948
−0.654 $3p^5[3d^2(^3F)]$ 0.597 $3p^53d(^3D)4s$ −0.311 $3p^5[3d^2(^1D)]$ −0.250 $3p^5[3d^2(^3P)]$ 0.162 $3p^53d(^1D)4s$	^2D	51.48	0.329
−0.980 $3p^53d(^1P)4s$	^2P	60.94	0.998

[a] Only coefficients greater than 0.12 are listed.

4. Conclusion

We have seen that R-matrix calculations for the excitation of Ti^{3+} employing a single-configuration target description lead to a significant overestimation in the excitation–autoionization cross section regardless of the number of $3p^53d^2$ channels included. Additional CI mixing of the $3p^2 \rightarrow 3d^2$ double-promotion type was necessary in order to obtain a better ionization cross section. By comparing to distorted-wave results, channel coupling effects were found to be small. The utility of performing unified R-matrix and distorted-wave calculations also lies in the identification of unphysical pseudo-resonances, arising in the R-matrix results, and accessing the validity of removing certain $(N + 1)$-electron configurations in the target description in order to avoid these pseudo-resonance problems. In the present case, it was found that removing the $3p^43d^4$ and $3p^33d^5$

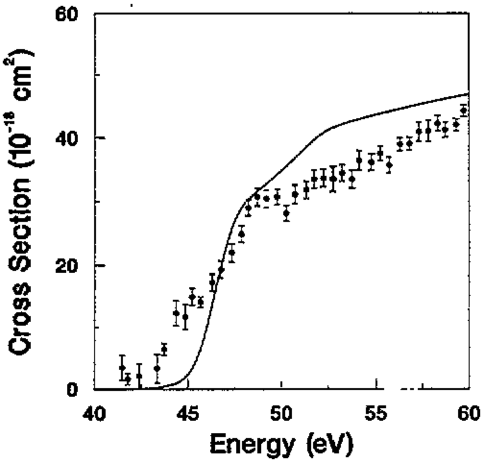

Figure 7. Electron-impact ionization cross section for Ti^{3+}; ——, 14-state *R*-matrix calculation with CI mixing in the target states, convoluted with a 2 eV FWHM Gaussian, and omitting correlating $N+1$-electron states (see text); ●, experimental measurements of Falk *et al* (1981, 1983).

configurations from the *R*-matrix wavefunction gave results consistent with non-resonant distorted-wave calculations above final threshold.

Acknowledgments

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