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# Calculated absolute electron-impact ionization cross sections for AlO, $Al_2O$, and $WO_x$ $(x=1-3)$

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The Deutsch–Märk (DM) formalism was used to calculate absolute electron impact ionization cross sections for the metal oxide molecules AlO, $Al_2O$, and $WO_x$ $(x=1-3)$. These molecules are important in materials research and they are also found as impurities in the plasma edge of fusion reactors. We also calculated ionization cross sections for the atoms Al and W. In the case of the Al-containing compounds, we find an unexpected ordering of the maximum ionization cross section $\sigma^{\max}$, $\sigma^{\max}(\mathrm{AlO})<\sigma^{\max}(\mathrm{Al})<\sigma^{\max}(\mathrm{Al_2O})$. Furthermore, the maximum ionization cross section for all four W-containing compounds W, WO, $WO_2$, and $WO_3$ is roughly the same with $\sigma^{\max}$ values in the range of $6-7\times10^{-16}\,\mathrm{cm}^2$. These findings can be understood by analyzing the DM calculations for these species as well as on the basis of semi-classical arguments. In addition, calculations using the semi-empirical modified additivity rule confirm the trends in the cross section ordering for, respectively, the Al-containing and W-containing compounds that was predicted by the DM formalism, at least qualitatively. © *2001 American Institute of Physics.*
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## I. INTRODUCTION

There is an urgent need for ionization cross sections in the mass spectrometric analysis of inorganic high temperature vapors. Knudsen effusion mass spectrometry (see Ref. 1, and references quoted therein) and high pressure mass spectrometry (see Ref. 2, and references quoted therein) are the most powerful methods for the analysis of such vapors. Numerous high temperature inorganic vapor species were identified by these methods for the first time and their partial pressures could be determined.[1,2] Ionization cross sections are necessary for the computation of partial pressures from the measured ion intensities which are used for the evaluation of thermodynamic data describing the stability of gaseous species. The data are incorporated in thermodynamic data bases and are widely used. The uncertainty originating from estimated ionization cross sections for the molecular species is generally high.[3,4] This applies also for the oxide species AlO(g), $Al_2O$(g), WO(g), and $WO_2$, as well as AlO(g) and $Al_2O$(g) which are major vapor species over $Al_2O_3$ base ceramics and tungsten. The computations presented in this article form the basis for mass spectrometric vaporization studies of $Al_2O_3$ and tungsten to determine more accurate values for the stability of the high temperature vapor species mentioned above. The species AlO(g), $Al_2O$(g), WO(g), and $WO_2$ are additionally important in fusion technology. Atomic tungsten and aluminum are among the atomic impurities in the plasma edge of fusion reactors.[5] In the presence of the omnipresent impurity oxygen,[5] the various Al– and W–oxygen compounds (AlO, $Al_2O$, WO, $WO_2$, and $WO_3$) have to be considered as possible molecular impurities as well.[5]

In this article, we present the results of the application of the Deutsch–Märk (DM) formalism to the calculation of ionization cross sections for the Al-containing molecules AlO, and $Al_2O$ and for the W-containing molecules $WO_x$ $(x=1-3)$. We also calculated ionization cross sections for the atoms Al and W. The ordering of the maximum in the calculated ionization cross sections $\sigma^{\max}$ for the Al-containing species exhibits a counterintuitive ordering, $\sigma^{\max}(\mathrm{AlO})<\sigma^{\max}(\mathrm{Al})<\sigma^{\max}(\mathrm{Al_2O})$. Furthermore, the maximum ionization cross section for the four W-containing compounds W, WO, $WO_2$, and $WO_3$ is roughly the same with a value in the range of $6-7\times10^{-16}\,\mathrm{cm}^2$, a finding that is also not expected intuitively. An attempt is made to explain these findings by analyzing the DM calculations for these species as well as on the basis of semi-classical arguments. In addition, we carried out calculations using the semi-empirical modified additivity rule (MAR) which confirmed the trends in the cross section ordering for, respectively, the Al-containing

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TABLE I. Parameters $a$, $b$, $c$, and $d$ for the energy dependent function in Eq. (2) for $s$, $p$, $d$ and $f$ electrons.

| | | | | |
|---|---|---|---|---|
| $s$ electrons: | $a=1.06$ | $b=0.23$ | $c=1$ | $d=1.1$ |
| $p$ electrons: | $a=2$ | $b=1$ | $c=1$ | $d=1$ |
| $d$ electrons: | $a=3/2$ | $b=3$ | $c=2/3$ | $d=1$ |
| $f$ electrons: | $a=3/2$ | $b=1$ | $c=2/3$ | $d=1$ |

and W-containing compounds obtained from the DM formalism, at least qualitatively.

## II. THEORETICAL BACKGROUND

A detailed discussion of the DM formalism as applied to molecules can be found in the recent review of Deutsch *et al.*[6] to which we refer the reader for an in-depth discussion of the DM method. Briefly, the DM formula for the calculation of the absolute electron-impact ionization cross section $\sigma$ of an atom has the form

$$\sigma=\sum_{n,l} g_{nl}\pi(r_{nl})^2\xi_{nl}\cdot f(U), \tag{1}$$

where $(r_{nl})^2$ is the radius of maximum radial density of the atomic subshell characterized by the quantum numbers $n$ and $l$ (column 1 in the tables of Desclaux[7]), $\xi_{nl}$ refers to the number of atomic electrons in the $(n,l)$ subshell, and the $g_{nl}$ are appropriately chosen weighting factors which are given in Ref. 6. The function $f(U)$ describes the energy dependence of the ionization cross section where $U$ is the reduced collision energy, $U=E/E_{nl}$. $E$ denotes the energy of the incident electron and $E_{nl}$ refers to the ionization energy in the $(n,l)$ subshell. The function $f(U)$ has the explicit form

$$\begin{aligned} f(U)=d(1/U)[(U-1)/(U+1)]^a\{b+c[1-(1/2U)]\\ \times\ln[2.7+(U-1)^{0.5}]\}, \end{aligned} \tag{2}$$

where the parameters $a$, $b$, $c$, and $d$ have different values for $s$, $p$, $d$, and $f$ electrons as one might expect on the basis of the different angular shapes of atomic $s$, $p$, $d$, and $f$ orbitals. Table I summarizes the values for the parameters $a$, $b$, $c$, and $d$ for $s$, $p$, $d$, and $f$ electrons, respectively. In the case of molecular targets, it was found advantageous[6] to express the molecular ionization cross section in terms of the atomic cross section formula of Eq. (1). This requires a Mulliken population analysis[8] or an equivalent method that expresses the molecular orbitals in terms of the atomic orbitals of the constituent atoms and determines the atomic orbital populations.

## III. RESULTS AND DISCUSSION

### A. Calculations using the DM formalism

The calculations presented in this article involve several metal oxide molecules. Different atomic basis sets and quantum chemical methods were used to determine the molecular geometries, the atomic orbital coefficients (orbital populations), and the ionization energies of the various molecules. Since no experimentally determined ionization cross sections for atomic tungsten (W) are available in the literature to the best of our knowledge, we also carried out a DM calculation for W using the original DM formula of Eq. (1). The quantum chemical information together with all parameters required to carry out the DM calculations for the five molecules presented in this publication are listed in tabular form in Tables I–VI. We note that a comparison of the calculated lowest ionization energies listed in Tables I–VI with known experimental values[9] shows that the Mulliken population analyses reproduce the experimental values very well for AlO and $Al_2O$, and reasonably well for $WO_3$, but that there are discrepancies in the case of WO and $WO_2$ (see discussion below).

TABLE II. Atomic orbital populations and other parameters required for the DM calculation of the ionization cross section of AlO. Listed are the effective electron population $\xi_{nl}$ in the respective $(n,l)$ subshells, the binding energies $E_{nl}$, the corresponding weighting factors $g_{nl}$, the radii $r_{nl}$ (Ref. 7), and the atomic orbital type. We note that only the outermost five molecular orbitals have been considered, since contributions from the remaining six core molecular orbitals to the ionization cross section are negligible. The calculation of the Al–O distance and of the $E_{nl}$ was performed with the MP2 method using the aug-cc-pVQZ basis set (Ref. 18). The atomic orbital populations were derived from restricted open Hartree–Fock (ROHF) calculations with the conduction-electron polarization (CEP)-4G basis set and effective core potentials (Ref. 19).

| $\xi_{nl}$ | $E_{nl}$ (in eV) | $g_{nl}$ | $r_{nl}$ (in $10^{-9}$ cm) | Atomic orbital | Molecular orbital (MO) No. |
|---|---|---|---|---|---|
| 0.034 | 9.64 | 1.452 | 11.09 | Al 3$s$ | 11 |
| 0.064 | 9.64 | 3.268 | 14.24 | Al 3$p$ | |
| 0.027 | 9.64 | 2.075 | 4.63 | O 2$s$ | |
| 0.875 | 9.64 | 3.112 | 4.41 | O 2$p$ | |
| 1.550 | 14.24 | 0.983 | 11.09 | Al 3$s$ | 10 and 9 |
| 0.462 | 14.24 | 2.212 | 14.24 | Al 3$p$ | |
| 0.050 | 14.24 | 1.405 | 4.63 | O 2$s$ | |
| 1.938 | 14.24 | 2.107 | 4.41 | O 2$p$ | |
| 0.184 | 18.07 | 1.743 | 14.24 | Al 3$p$ | 8 |
| 1.816 | 18.07 | 1.107 | 4.41 | O 2$p$ | |
| 0.126 | 35.70 | 0.392 | 11.09 | Al 3$s$ | 7 |
| 0.168 | 35.70 | 0.882 | 14.24 | Al 3$p$ | |
| 1.670 | 35.70 | 0.560 | 4.63 | O 2$s$ | |
| 0.036 | 35.70 | 0.840 | 4.41 | O 2$p$ | |

Figure 1 shows the calculated ionization cross sections for AlO and $Al_2O$ together with the atomic Al ionization cross section. We note that in the case of Al the calculated ionization cross sections and the measured cross sections[10] are in good agreement. The cross section ordering depicted in Fig. 1 is noteworthy. We find a surprising ordering of the maximum ionization cross section values $\sigma^{\max}$, $\sigma^{\max}(\mathrm{AlO})<\sigma^{\max}(\mathrm{Al})<\sigma^{\max}(\mathrm{Al_2O})$, i.e., the maximum ionization cross section of the molecule AlO is smaller than the maximum atomic Al ionization cross section by almost a factor of 2, whereas the $Al_2O$ cross section exceeds the Al cross section by about 25% and the AlO cross section by a factor of 2.5. In fact, the entire cross section curves show the above ordering qualitatively for all electron energies above about 20 eV.

This ordering can be understood by analyzing the DM cross section formula. Table II shows that AlO has an ionization threshold of 9.64 eV (for the outermost valence orbital) which is almost 4 eV higher than the ionization energy of atomic Al [which is about 6 eV for the lone electron in the

TABLE III. Atomic orbital populations and other parameters required for the DM calculation of the ionization cross section of $Al_2O$. Listed are the effective electron population $\xi_{nl}$ in the respective $(n,l)$ subshells, the binding energies $E_{nl}$, the corresponding weighting factors $g_{nl}$, the radii $r_{nl}$ (Ref. 7), and the atomic orbital type. We note that only the outermost six molecular orbitals have been considered, since contributions from the remaining 11 core molecular orbitals to the ionization cross section are negligible. The calculation of the geometry of $Al_2O$ and of the $E_{nl}$ was performed with the MP2 method and the aug-cc-pVTZ basis set (Ref. 18). The atomic orbital populations were derived from restricted Hartree–Fock (RHF) calculations with the (CEP)-4G basis set and effective core potentials (Ref. 19).

| $\xi_{nl}$ | $E_{nl}$ (in eV) | $g_{nl}$ | $r_{nl}$ (in $10^{-9}$ cm) | Atomic orbital | MO No. |
|---|---|---|---|---|---|
| 0.950 | 8.10 | 1.728 | 11.09 | Al 3$s$ | 17 |
| 0.840 | 8.10 | 3.889 | 14.24 | Al 3$p$ | |
| 0.210 | 8.10 | 3.704 | 4.41 | O 2$p$ | |
| 1.730 | 9.09 | 1.540 | 11.09 | Al 3$s$ | 16 |
| 0.220 | 9.09 | 3.465 | 14.24 | Al 3$p$ | |
| 0.040 | 9.09 | 2.200 | 4.63 | O 2$s$ | |
| 0.010 | 9.09 | 3.300 | 4.41 | O 2$p$ | |
| 0.008 | 13.08 | 1.072 | 11.09 | Al 3$s$ | 15 and 14 |
| 0.528 | 13.08 | 2.412 | 14.24 | Al 3$p$ | |
| 0.006 | 13.08 | 1.531 | 4.63 | O 2$s$ | |
| 3.458 | 13.08 | 2.297 | 4.41 | O 2$p$ | |
| 0.600 | 16.97 | 0.825 | 11.09 | Al 3$s$ | 13 |
| 0.064 | 16.97 | 1.856 | 14.24 | Al 3$p$ | |
| 1.336 | 16.97 | 1.768 | 4.41 | O 2$p$ | |
| 0.136 | 34.02 | 0.412 | 11.09 | Al 3$s$ | 12 |
| 0.244 | 34.02 | 0.926 | 14.24 | Al 3$p$ | |
| 1.620 | 34.02 | 0.588 | 4.63 | O 2$s$ | |

TABLE IV. Atomic orbital populations and other parameters required for the DM calculation of the ionization cross section of WO. Listed are the effective electron population $\xi_{nl}$ in the respective $(n,l)$ subshells, the binding energies $E_{nl}$, the corresponding weighting factors $g_{nl}$, the radii $r_{nl}$ (Ref. 7) and the atomic orbital type. We note that only the outermost ten molecular orbitals have been considered, since contributions from the remaining 31 core molecular orbitals to the ionization cross section are negligible. The calculation of the W–O distance and of the $E_{nl}$ was performed with the RHF method and the SDD basis sets and effective core potentials (Refs. 20 and 21). The atomic orbital populations were derived from ROHF calculations with the CEP-4G basis set and effective core potentials (Ref. 19).

| $\xi_{nl}$ | $E_{nl}$ (in eV) | $g_{nl}$ | $r_{nl}$ (in $10^{-9}$ cm) | Atomic orbital | MO No. |
|---|---|---|---|---|---|
| 0.120 | 6.41 | 1.170 | 5.15 | W 5$s$ | 41 and 40 |
| 0.002 | 6.41 | 2.028 | 5.94 | W 5$p$ | |
| 3.220 | 6.41 | 1.381 | 8.02 | W 5$d$ | |
| 0.620 | 6.41 | 0.936 | 14.76 | W 6$s$ | |
| 0.012 | 6.41 | 3.120 | 4.63 | O 2$s$ | |
| 0.026 | 6.41 | 4.680 | 4.41 | O 2$p$ | |
| 0.020 | 12.28 | 1.059 | 5.94 | W 5$p$ | 38 and 39 |
| 1.024 | 12.28 | 0.721 | 8.02 | W 5$d$ | |
| 0.116 | 12.28 | 0.489 | 14.76 | W 6$s$ | |
| 2.840 | 12.28 | 2.443 | 4.41 | O 2$p$ | |
| 0.016 | 13.06 | 0.576 | 5.15 | W 5$s$ | 37 |
| 0.016 | 13.06 | 0.995 | 5.94 | W 5$p$ | |
| 0.446 | 13.06 | 0.678 | 8.02 | W 5$d$ | |
| 0.048 | 13.06 | 0.459 | 14.76 | W 6$s$ | |
| 0.080 | 13.06 | 1.531 | 4.63 | O 2$s$ | |
| 1.396 | 13.06 | 2.297 | 4.41 | O 2$p$ | |
| 0.018 | 31.93 | 0.235 | 5.15 | W 5$s$ | 36 |
| 0.100 | 31.93 | 0.407 | 5.94 | W 5$p$ | |
| 0.318 | 31.93 | 0.277 | 8.02 | W 5$d$ | |
| 0.148 | 31.93 | 0.188 | 14.76 | W 6$s$ | |
| 1.404 | 31.93 | 0.626 | 4.63 | O 2$s$ | |
| 0.012 | 31.93 | 0.937 | 4.41 | O 2$p$ | |
| 3.844 | 50.39 | 0.258 | 5.94 | W 5$p$ | 35 and 34 |
| 0.148 | 50.39 | 0.119 | 14.76 | W 6$s$ | |
| 0.008 | 50.39 | 0.595 | 4.41 | O 2$p$ | |
| 1.818 | 52.32 | 0.249 | 5.94 | W 5$p$ | 33 |
| 0.002 | 52.32 | 0.169 | 8.02 | W 5$d$ | |
| 0.080 | 52.32 | 0.115 | 14.76 | W 6$s$ | |
| 0.052 | 52.32 | 0.382 | 4.63 | O 2$s$ | |
| 0.048 | 52.32 | 0.573 | 4.41 | O 2$p$ | |
| 1.466 | 91.71 | 0.082 | 5.51 | W 5$s$ | 32 |
| 0.452 | 91.71 | 0.097 | 8.02 | W 5$d$ | |
| 0.076 | 91.71 | 0.065 | 14.76 | W 6$s$ | |
| 0.006 | 91.71 | 0.327 | 4.41 | O 2$p$ | |

outermost Al 3$s$ subshell]. Moreover, the ionization energy of the second outermost AlO molecular orbital (14.24 eV) is also more than 3 eV higher than the ionization energy of the second outermost atomic subshell, Al 3$p$, of about 11 eV. As the DM formalism mandates that the product $(E_{nl} \cdot g_{nl})$ of ionization energy $E_{nl}$ and weighting factor $g_{nl}$, the so-called ''reduced weighting factor,'' is a constant for any given atomic subshell $(n,l)$,[6] the shift in the ionization energies for the two outermost orbitals by more than 3 eV in each case means that the weighting factors for the Al 3$s$ and Al 3$p$ contributions to the ionization cross section for AlO are significantly smaller than the contributions of the same subshells to the atomic Al ionization cross section. In addition, there is a significant atomic oxygen contribution, primarily O 2$p$, in the atomic orbital populations of the two outermost molecular AlO orbitals. These oxygen orbitals have significantly smaller radii than the Al orbitals. Since the calculated ionization cross section depends on $(r_{nl})^2$ [see Eq. (1)], the oxygen orbitals contribute much less to the AlO ionization cross section than the Al orbitals. This explains why the calculated AlO ionization cross section is much smaller than the atomic Al ionization cross section.

Similar arguments can be used to understand why the $Al_2O$ ionization cross section is much larger (by a factor of 2.5!) than the AlO ionization cross section. $Al_2O$ has an ionization energy that is 1.5 eV lower compared to that of AlO. In addition, there are five molecular orbitals with ionization energies below 17 eV, which account for most of the $Al_2O$ ionization cross section. The electrons in these orbitals have comparatively large weighting factors. Moreover, when compared to AlO, the oxygen contributions in the two outermost molecular orbitals of $Al_2O$ are much smaller than the corresponding oxygen contributions in the two outermost molecular orbitals of AlO. This explains why the $Al_2O$ ionization cross section is much larger than the AlO ionization cross section. On the other hand, the facts that (i) $Al_2O$ has a larger ionization energy than Al and that (ii) the outermost molecular orbitals have some oxygen contributions in their molecular orbitals explain why the $Al_2O$ ionization cross section is only about 30% larger than the atomic Al ioniza-

TABLE V. Atomic orbital populations and other parameters required for the DM calculation of the ionization cross section of $WO_2$. Listed are the effective electron population $\xi_{nl}$ in the respective $(n,l)$ subshells, the binding energies $E_{nl}$, (Ref. 7), the corresponding weighting factors $g_{nl}$, the radii $r_{nl}$ (Ref. 7) and the atomic orbital type. We note that only the outermost 13 molecular orbitals have been considered, since contributions from the remaining 32 core molecular orbitals to the ionization cross section are negligible. The optimization of the $WO_2$ geometry was performed by B3LYP calculations with the SDD basis set (Refs. 20 and 21), while the same basis set and the MP2 method were used to calculate the $E_{nl}$. The atomic orbital populations were derived from RHF calculations with the CEP-4G basis set and effective core potentials (Ref. 19).

| $\xi_{nl}$ | $E_{nl}$ (in eV) | $g_{nl}$ | $r_{nl}$ (in $10^{-9}$ cm) | Atomic orbital | MO No. |
|---|---|---|---|---|---|
| 0.046 | 11.70 | 1.111 | 5.94 | W 5*p* | 45 and 44 |
| 0.608 | 11.70 | 0.513 | 14.76 | W 6*s* | |
| 3.346 | 11.70 | 2.564 | 4.41 | O 2*p* | |
| 1.138 | 11.84 | 0.633 | 5.94 | W 5*p* | 43 |
| 1.320 | 11.84 | 0.748 | 8.02 | W 5*d* | |
| 0.418 | 11.84 | 0.507 | 14.76 | W 6*s* | |
| 0.016 | 11.84 | 0.689 | 4.63 | O 2*s* | |
| 0.112 | 11.84 | 2.534 | 4.41 | O 2*p* | |
| 0.052 | 12.20 | 1.066 | 5.94 | W 5*p* | 42 |
| 0.052 | 12.20 | 0.492 | 14.76 | W 6*s* | |
| 0.020 | 12.20 | 1.634 | 4.63 | O 2*s* | |
| 1.872 | 12.20 | 2.459 | 4.41 | O 2*p* | |
| 1.942 | 14.35 | 0.617 | 8.02 | W 5*d* | 41 and 40 |
| 2.058 | 14.35 | 2.091 | 4.41 | O 2*p* | |
| 0.010 | 16.14 | 0.465 | 5.51 | W 5*s* | 39 |
| 0.514 | 16.14 | 0.548 | 8.02 | W 5*d* | |
| 0.006 | 16.14 | 0.372 | 14.76 | W 6*s* | |
| 0.148 | 16.14 | 1.234 | 4.63 | O 2*s* | |
| 1.322 | 16.14 | 1.859 | 4.41 | O 2*p* | |
| 0.092 | 32.17 | 0.948 | 5.94 | W 5*p* | 38 |
| 0.282 | 32.17 | 0.933 | 14.76 | W 6*s* | |
| 1.622 | 32.17 | 0.468 | 4.63 | O 2*s* | |
| 0.004 | 32.17 | 1.010 | 4.41 | O 2*p* | |
| 0.022 | 34.53 | 0.217 | 5.51 | W 5*s* | 37 |
| 0.560 | 34.53 | 0.256 | 8.02 | W 5*d* | |
| 0.078 | 34.53 | 0.174 | 14.76 | W 6*s* | |
| 1.296 | 34.53 | 0.579 | 4.63 | O 2*s* | |
| 0.044 | 34.53 | 0.869 | 4.41 | O 2*p* | |
| 3.864 | 55.38 | 0.235 | 5.94 | W 5*p* | 36 and 35 |
| 0.128 | 55.38 | 0.108 | 14.76 | W 6*s* | |
| 0.008 | 55.38 | 0.542 | 4.41 | O 2*p* | |
| 1.838 | 56.24 | 0.231 | 5.94 | W 5*p* | 34 |
| 0.078 | 56.24 | 0.107 | 14.76 | W 6*s* | |
| 0.036 | 56.24 | 0.356 | 4.63 | O 2*s* | |
| 0.048 | 56.24 | 0.533 | 4.41 | O 2*p* | |
| 1.478 | 96.83 | 0.078 | 5.51 | W 5*s* | 33 |
| 0.442 | 96.83 | 0.091 | 8.02 | W 5*d* | |
| 0.076 | 96.83 | 0.062 | 14.76 | W 6*s* | |
| 0.004 | 96.83 | 0.310 | 4.41 | O 2*p* | |

TABLE VI. Atomic orbital populations and other parameters required for the DM calculation of the ionization cross section of $WO_3$. Listed are the effective electron population $\zeta_{nl}$ in the respective $(n,l)$ subshells, the binding energies $E_{nl}$, the corresponding weighting factors $g_{nl}$, the radii $r_{nl}$ (Ref. 7), and the atomic orbital type. We note that only the outermost 16 molecular orbitals have been considered, since contributions from the remaining 33 core molecular orbitals to the ionization cross section are negligible. The optimization of the $WO_3$ geometry was performed by B3LYP calculations with the SDD basis set (Refs. 20 and 21), while the same basis set and the MP2 method were used to calculate the $E_{nl}$. The atomic orbital populations were derived from RHF calculations with the CEP-4G basis set and effective core potentials (Ref. 19).

| $\zeta_{nl}$ | $E_{nl}$ (in eV) | $g_{nl}$ | $r_{nl}$ (in $10^{-9}$ cm) | Atomic orbital | MO No. |
|---|---|---|---|---|---|
| 0.034 | 12.98 | 1.002 | 5.94 | W 5*p* | 49 |
| 0.402 | 12.98 | 0.462 | 14.76 | W 6*s* | |
| 1.564 | 12.98 | 2.311 | 4.41 | O 2*p* | |
| 2.000 | 14.04 | 2.137 | 4.41 | O 2*p* | 48 |
| 0.088 | 14.19 | 0.916 | 5.94 | W 5*p* | 47 and 46 |
| 0.338 | 14.19 | 0.624 | 8.02 | W 5*d* | |
| 0.096 | 14.19 | 0.423 | 14.76 | W 6*s* | |
| 0.032 | 14.19 | 1.409 | 4.63 | O 2*s* | |
| 3.446 | 14.19 | 2.114 | 4.41 | O 2*p* | |
| 1.996 | 15.63 | 0.566 | 8.02 | W 5*d* | 45 and 44 |
| 2.004 | 15.63 | 1.919 | 4.41 | O 2*p* | |
| 0.044 | 16.55 | 0.453 | 5.51 | W 5*s* | 43 |
| 0.322 | 16.55 | 0.535 | 8.02 | W 5*d* | |
| 0.016 | 16.55 | 0.363 | 14.76 | W 6*s* | |
| 0.126 | 16.55 | 1.209 | 4.63 | O 2*s* | |
| 1.492 | 16.55 | 1.813 | 4.41 | O 2*p* | |
| 1.134 | 17.70 | 0.500 | 8.02 | W 5*d* | 42 and 41 |
| 0.212 | 17.70 | 0.339 | 14.76 | W 6*s* | |
| 0.138 | 17.70 | 1.230 | 4.63 | O 2*s* | |
| 2.516 | 17.70 | 1.695 | 4.41 | O 2*p* | |
| 0.180 | 34.83 | 0.373 | 5.94 | W 5*p* | 40 and 39 |
| 0.582 | 34.83 | 0.254 | 8.02 | W 5*d* | |
| 0.382 | 34.83 | 0.172 | 14.76 | W 6*s* | |
| 2.832 | 34.83 | 0.574 | 4.63 | O 2*s* | |
| 0.024 | 34.83 | 0.861 | 4.41 | O 2*p* | |
| 0.042 | 36.17 | 0.207 | 5.51 | W 5*s* | 38 |
| 0.374 | 36.17 | 0.245 | 8.02 | W 5*d* | |
| 0.120 | 36.17 | 0.166 | 14.76 | W 6*s* | |
| 1.428 | 36.17 | 0.553 | 4.63 | O 2*s* | |
| 0.036 | 36.17 | 0.829 | 4.41 | O 2*p* | |
| 1.930 | 57.98 | 0.224 | 5.94 | W 5*p* | 37 |
| 0.064 | 57.98 | 0.104 | 14.76 | W 6*s* | |
| 0.006 | 57.98 | 0.518 | 4.41 | O 2*p* | |
| 3.656 | 58.55 | 0.222 | 5.94 | W 5*p* | 36 and 35 |
| 0.004 | 58.55 | 0.151 | 8.02 | W 5*d* | |
| 0.164 | 58.55 | 0.103 | 14.76 | W 6*s* | |
| 0.078 | 58.55 | 0.342 | 4.63 | O 2*s* | |
| 0.098 | 58.55 | 0.512 | 4.41 | O 2*p* | |
| 1.462 | 99.48 | 0.076 | 5.51 | W 5*s* | 34 |
| 0.450 | 99.48 | 0.089 | 8.02 | W 5*d* | |
| 0.076 | 99.48 | 0.060 | 14.76 | W 6*s* | |
| 0.012 | 99.48 | 0.302 | 4.41 | O 2*p* | |

tion cross section rather than by a factor of 2 or more which is what one might expect intuitively.

A semi-classical explanation of the unexpected cross section ordering for Al, AlO, and $Al_2O$ utilizes the calculated atomic orbital populations (Tables II and III) in connection with the fact that the atomic Al ionization cross section is much larger (by almost a factor of 6!) than the atomic oxygen ionization cross section. The dominant contributions to the AlO ionization cross section arise from molecular orbitals with significant oxygen atomic population, primarily

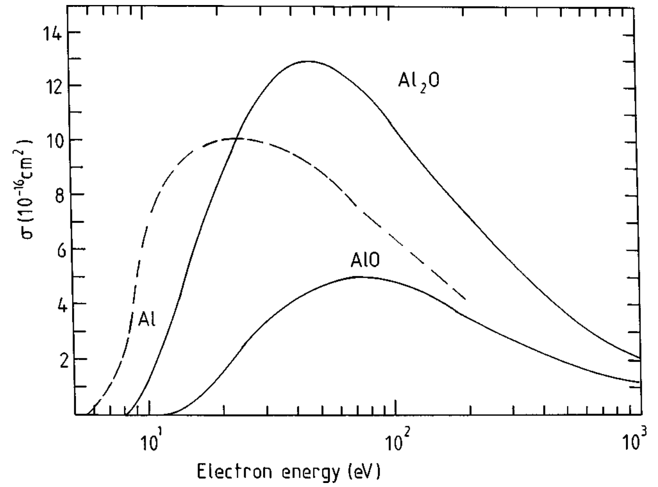

FIG. 1. Calculated electron impact ionization cross section of Al, AlO, and $Al_2O$ from threshold to 1000 eV using the DM formalism.

O 2*p*. Since the O atom has an ionization cross section which is much smaller than that of the Al atom, the resultant AlO cross section is much smaller than the atomic Al ionization cross section. In contrast to AlO, the two outermost $Al_2O$ orbitals have significant Al atomic populations, so that the large Al ionization cross section dominates the $Al_2O$ cross section. However, the $Al_2O$ molecular orbitals labeled number 12–15 in Table III have appreciable atomic oxygen populations, which explains why the $Al_2O$ ionization cross section is only slightly larger than the atomic Al ionization cross section.

The situation is quite different for atomic tungsten (W) and the $WO_x$ ($x=1-3$) molecules. As can be seen in Fig. 2, all four species have roughly the same maximum ionization cross section with peak values in the range $6-7\times10^{-16}\,\mathrm{cm}^2$. Furthermore, the energy dependence of the calculated W and WO ionization cross sections, on the one hand, and that of the $WO_2$ and $WO_3$ ionization cross sections, on the other hand, are very similar. The W and WO cross sections peak at around 35 eV, whereas the $WO_2$ and $WO_3$ cross sections reach their maximum at higher energies, 60 eV ($WO_2$) and 75 eV ($WO_3$). This behavior is not unexpected, if one assumes that the well known ''rule of thumb'' [11] which stipulates that atomic ionization cross sections reach their maximum at impact energies that are a few times the ionization energy is also applicable to molecular ionization cross sections. We note that there are no measured values of the W ionization cross section to the best of our knowledge. The W ionization cross section for W shown in Fig. 2 has also been calculated using the DM formalism. Even though the calculated ionization energy of WO (6.4 eV) is about 1.5 eV lower than that of atomic W (8.1 eV), which results in larger weighting factors for WO, three of the five outermost WO orbitals have atomic populations with significant oxygen contributions (see Table IV). Because of the smaller radii of the O 2*s* and O 2*p* orbitals compared to the W orbitals, in particular compared to W 5*d* and W 6*s*, the net result is a WO ionization cross section that is only marginally larger than the W ionization cross section. Both $WO_2$ and $WO_3$ have calculated ionization energies that are 5–6 eV higher than the ionization energy of WO and, consequently, $WO_2$ and $WO_3$ have smaller weighting factors. Furthermore, the outermost $WO_2$ and $WO_3$ orbitals have atomic populations with appreciable oxygen contributions. This explains why their respective ionization cross sections are not larger than the WO ionization cross section, but in fact are even somewhat smaller.

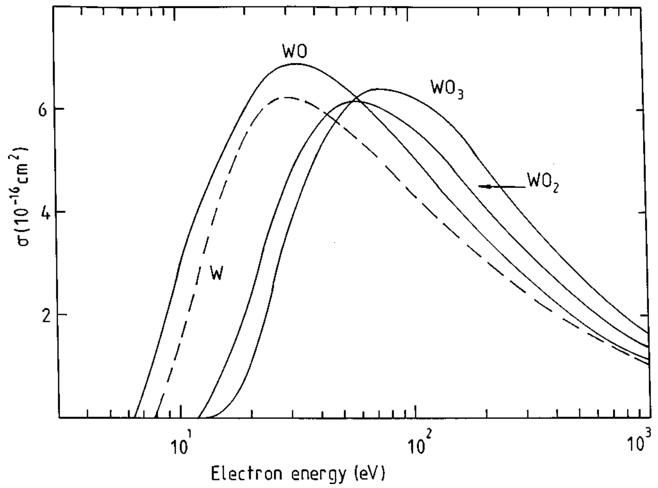

FIG. 2. Calculated electron impact ionization cross section of W and $WO_x$ ($x=1-3$) from threshold to 1000 eV using the DM formalism.

As mentioned above, the lowest ionization energies for WO and $WO_2$ that were calculated in the present work (Tables IV and V) differ from the experimentally determined ionization energies for these molecules.[9] In the case of $WO_2$, the difference between the calculated value (11.7 eV) and the measured value (9.5 eV with a 0.5 eV uncertainty, which is the average value of five individual measurements)[9] is about 2 eV. Substitution of the experimental value for the calculated value in the ionization cross section calculation results in a cross section curve with a maximum value of $6.4\times10^{-16}\,\mathrm{cm}^2$ at 50 eV compared to a maximum value of $6.1\times10^{-16}\,\mathrm{cm}^2$ at 70 eV. This is a fairly minor change which does not affect the validity of the statements made in the previous paragraphs in a substantial fashion. For WO, the difference between the calculated ionization energy of 6.4 eV and the measured ionization energy of 9.1 eV (which is the result of a single measurement with a comparatively large uncertainty of 1 eV)[9] is somewhat larger. The effect of substituting the measured value for the calculated value in the ionization cross section calculation is a shift of the maximum value from $6.8\times10^{-16}\,\mathrm{cm}^2$ at 30 eV to $5.9\times10^{-16}\,\mathrm{cm}^2$ at 40 eV. This would reduce the maximum WO ionization cross section to a value slightly below the maximum atomic W ionization cross section, but it would also not affect the general validity of the previous conclusions about the ionization cross sections of W and the $WO_x$ molecules. Last, we note that the calculated ionization energy for $WO_3$ (13 eV, see Table VI) is in satisfactory agreement with the experimental value of 12.2 eV (which has 0.5 eV uncertainty and represents the average of six individual measurements).[9]

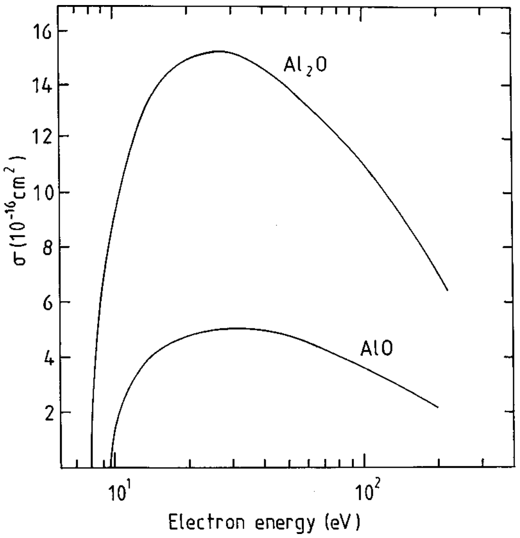

FIG. 3. Calculated electron impact ionization cross section of AlO and $Al_2O$ from threshold to 200 eV using the MAR formalism.

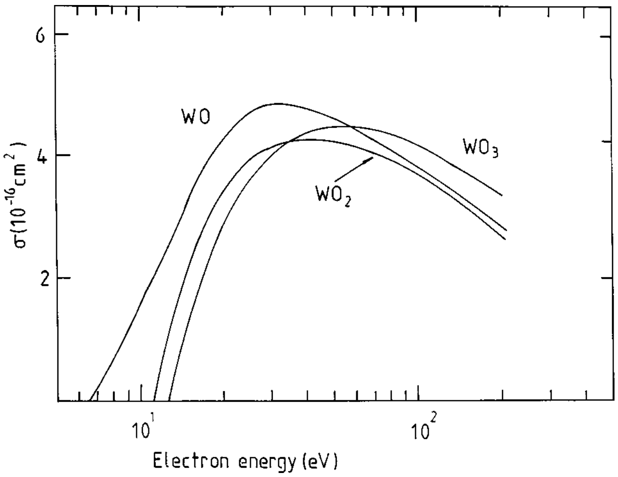

FIG. 4. Calculated electron impact ionization cross section of $WO_x$ ($x=1-3$) from threshold to 200 eV using the MAR formalism.

## B. Calculations using the MAR

We also carried out ionization cross section calculations using the semi-empirical MAR. The MAR has been described in detail in recent publications[12,13] to which we refer the reader for further information. Briefly, additivity rules in their simplest form stipulate that the ionization cross section of a molecule is given as the sum of the atomic ionization cross sections of the constituent atoms of the molecule. Several variants of this simple additivity rule incorporated ways to account for molecular bonding. The MAR utilizes sets of empirically determined weighting factors to account for molecular bonding for various families of molecules with the same sum formula, i.e., for molecules of the form $AB_x$, $A_xB_y$, and $A_xB_yC_z$. When applied to AlO and $Al_2O$, the MAR formalism reproduces the respective cross sections calculated with the DM method to within about 10%–15% in terms of the maximum cross section value (Fig. 3) and thus confirms the cross section ordering obtained from the DM calculations. In the case of $WO_x$, the MAR calculations confirm the prediction from the DM calculation that all three molecules have essentially the same maximum ionization cross section value. However, the absolute MAR cross sections are smaller than the DM cross sections by about 30%. It is interesting to note that a similar 30% discrepancy in the absolute ionization cross section values obtained from the MAR method (Fig. 4) and the DM formalism, respectively, was also found recently for the molecule $WF_6$.[14]

Finally, we mention that another semi-rigorous method for the calculation of molecular electron-impact ionization cross sections was developed by Kim and co-workers, the so-called binary-encounter bethe (BEB) model.[15] Similar to the DM method, the BEB model was derived from a method that was initially developed for the calculation of atomic ionization cross sections, the binary-encounter dipole method.[16] The BEB method has been applied successfully to the calculation of ionization cross sections of more than 30 molecules and radicals.[17] As shown in the recent review of Deutsch *et al.*,[6] the DM formalism and the BEB formalism predict ionization cross sections which are in very good to satisfactory agreement with each other and with experimental data for most target species where results from both calculations and reliable experimental data are available. To the best of our knowledge, no BEB calculations have been reported for the species AlO, $Al_2O$, and $WO_x$ ($x=1-3$).

## IV. SUMMARY

We applied the DM formalism in a series of calculations of absolute electron-impact ionization cross sections for the oxides AlO, $Al_2O$, $WO_x$ ($x=1-3$). In the case of AlO and $A_2O$ we found that the AlO ionization cross section is much smaller than the atomic Al ionization cross section, whereas the $Al_2O$ ionization cross section is much larger than the AlO cross section and somewhat larger than the Al cross section. In the case of $WO_x$, all three molecules have maximum ionization cross section values that are roughly the same and that are also very similar to the atomic W ionization cross section. These findings can be understood by analyzing the DM calculations for these species as well as on the basis of semi-classical arguments. In addition, calculations using the semi-empirical MAR confirm the trends in the cross section ordering for, respectively, the Al-containing and W-containing compounds that was predicted by the DM formalism, at least qualitatively.

## ACKNOWLEDGMENTS

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