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Electron-impact ionization cross sections of small molecules containing Fe and Cr*

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Abstract

We present the electron-impact ionization cross sections (EICSs) of iron and chromium hydrides, nitrides, and oxides. The motivation of this work stems from the fact that chemical sputtering from a steel surface exposed to a hot plasma can create these molecules which in turn influence the composition and energy balance of the plasma. The latter influence is quantified by the EICS which we derive by using two semi-empirical methods which can be employed in the relevant energy range of 10–1000 eV. They are important molecular properties for plasma- and materials science. We discuss the foundations of the methods and present the cross sections of the high- and low-spin states of the species in their neutral ground states and of their cations.

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Choosing appropriate steels for future fusion reactors is both an important and difficult decision. One key requirement is a low activation [1, 2] by neutrons. Components of a reactor can also become radioactive for many years due to tritium insertion. Besides low activation, other desired features of such steels are high temperature and corrosion resistance, structural insensitivity to neutron irradiation and fracture toughness [2, 3]. Elements such as Mo, Nb and Ni cannot be used and are replaced with low activation materials, e.g. W and Ta [4]. Other alloys containing metallic elements such as V, Cr, and Ti have acceptable low activation properties. Apart from a low activation, mechanical properties and the production and processing technology of these wall materials are key factors [2]. Chromium based alloys, such as 12% Cr steels, have already been used for decades in conventional power plants and turbines [2] and their production and processing technologies are well established. These steels are normally referred to by their number within the EUROFER classification. To this date, little to nothing is known about

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* This work is dedicated to Enrico Clementi who pioneered the interdisciplinary use of quantum chemistry and computational modelling.

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the electron-impact ionization cross sections (EICSs) of atoms and small molecules sputtered by particles present in hot plasma from a steel surface. Knowing these cross sections is necessary because a layer of ionized impurities causes undesired effects on the plasma, for example by changing its energy balance [5]. This makes the reactor less efficient. Impurities are also transported by magnetic and electric fields inside the reactor chamber to other surfaces [5] where they can cause undesirable formation of deposits and alloys. While relevance to fusion plasma research is the main impetus for our work, knowledge of the EICS is also important in lighting and medical applications where lower energy plasmas are used.

Fe and Cr atoms can be sputtered chemically and physically from steels used as wall materials in fusion devices and can survive as atoms or form hydrides, oxides, and nitrides. The harsh conditions make the existence of larger molecules unlikely.

The EICSs are calculated for the neutral and cationic compounds. We use two semi-empirical methods, the binary-encounter-Bethe (BEB) [6, 7] and the Deutsch–Märk (DM) formalism [8]. Both methods are briefly described in section 2. While for low impact energies several quantum chemical methods exist to derive electron impact ionization cross sections more rigorously [9], for higher energy ranges semi-empirical approaches are the only tools available.

2. Methods

In this section we briefly describe the BEB and the DM method, both of which are used to calculate the EICSs. Despite the fact that both methods are based on the Born-Bethe approximation [8, 10], they differ substantially from one another. The Born-Bethe approximation is an extension of the Born approximation for lower incident energies of the incoming electron.

2.1. Binary-encounter-Bethe (BEB) method

Introduced by Kim and Rudd [11] for deriving EICSs, this method was presented as a simpler alternative to the binary-encounter-dipole (BED) model, which they also put forward the same year. Contrary to the BED method, BEB does not require the differential oscillator strengths of the subshells.

The total cross-section of an atom/molecule is given by the sum of contributions from each atomic/molecular orbital (AO/MO). The terms of this sum are a modified version of the Mott cross section. The formula developed by Mott [12] accurately predicts the cross sections of hard collisions between high energy free electrons (hence modified to account for bound electrons), in turn generalizing Rutherford's cross-section formula. It considers the spin of the colliding particles and thus the exchange interaction. An added term based on the Bethe theory takes care of the correct asymptotic dependence at high kinetic energies [11, 13].

For a molecule with N occupied orbitals (where α and β orbitals are distinguishable), the EICS as function of the kinetic energy T is:

$$\sigma_{\text{BEB}} = \sum_{k=1}^{N} \frac{H(t_k - 1) S_k}{t_k + u_k + 1} \left(\frac{\ln(t_k)}{2} \left(1 - \frac{1}{t_k^2} \right) + 1 - \frac{1}{t_k} - \frac{\ln(t_k)}{t_k + 1} \right),$$

(1)

where $t_k = T/B_k$, $u_k = U_k/B_k$, $S_k = 4\pi a_0^2 N_k R^2 / B_k^2$, H is the Heaviside step function, a_0 is the Bohr radius, R is the Rydberg energy, and B_k and U_k are the potential and average kinetic energies (respectively) of the kth occupied MO, and N_k is the number of electrons occupying the orbital k. For restricted calculations, where the orbitals for α and β electrons are identical, the factor N_k is always equal to 2, whereas for unrestricted calculations is equal to 1 since both α and β electrons of each shell are accounted for separately.

2.2. Deutsch–Märk (DM) method

Developed also in 1994, this semiclassical formalism was first used to estimate the absolute cross sections of single ionization by electron impact [14]. However, it has seen several improvements in the years afterwards [15]. Like in the BEB formalism, the total cross-section is a sum of partial cross sections, however, instead of taking the potential and kinetic energy of each occupied MO, the DM method relies on a population analysis (e.g. Mulliken population) to disentangle the contributions from the AOs of the atoms.

In 1964 Gryziński introduced the concept of a continuous velocity distribution $f: \mathbb{R}_0^+ \to \mathbb{R}_0^+$, for the bound electrons of an atom [16, 17], which he assumed to be of the form:

$$f(v_{n,l}) = \frac{1}{\bar{v}_{n,l}} \left(\frac{\bar{v}_{n,l}}{v_{n,l}} \right)^3 \exp \left(-\frac{\bar{v}_{n,l}}{v_{n,l}} \right),$$

(2)

where $v_{n,l}$ is the velocity of a bound electron with quantum numbers n and l, and $\bar{v}_{n,l}$ is its mean velocity, thus:

$$\int_0^{+\infty} v_{n,l} f(v_{n,l}) \, dv_{n,l} = \bar{v}_{n,l} \quad \text{and} \quad \int_0^{+\infty} f(v_{n,l}) \, dv_{n,l} = 1. \quad (3)$$

While this expression does not have a sound theoretical foundation, it allowed Gryziński to obtain a logarithmic asymptotic behaviour similar to Bethe's theory [16, 18]. After averaging with this distribution function, and based on several assumptions, Gryziński was able to arrive at a formula for the cross-section for ionization by light particles (in SI units, originally atomic units were used) [17, 19]:

$$\sigma_{\text{Gryz}}(u_{n,l}) = 4\pi a_0^2 \left(\frac{R}{E_{n,l}} \right)^2 g(u_{n,l}) \quad (4a)$$

$$g(u_{n,l}) = \frac{1}{u_{n,l}} \left(\frac{u_{n,l} - 1}{u_{n,l} + 1} \right)^{3/2}$$
$$\times \left(1 + \frac{2}{3} \left(1 - \frac{1}{2u_{n,l}} \right) \ln \left(e + (u_{n,l} - 1)^{1/2} \right) \right),$$

(4b)

where $u_{n,l} = E/E_{n,l}$ is the ratio between the kinetic energy of the incident electron and the biding energy of the electron on

the electronic shell with quantum numbers (n, l), a_0 is the Bohr radius, R is the Rydberg energy, and e is Euler's number.

Deutsch and Märk made this $g_{n,l}(u_{n,l})$ function more flexible by replacing the Bohr radius with $r_{n,l}$ where the electron density of the corresponding AO has its maximum [20]. They also found that replacing Gryziński's g function by similar functions depending on the type of the orbital (s, p, d or f) leads to a better agreement with experimental results [15, 21]. They defined these functions as:

$$g_{n,l}(u_{n,l}) = \frac{d}{u_{n,l}} \left(\frac{u_{n,l} - 1}{u_{n,l} + 1} \right)^a$$
$$\times \left(b + c \left(1 - \frac{1}{2u_{n,l}} \right) \ln \left(e + (u_{n,l} - 1)^{1/2} \right) \right),$$
(5)

where the coefficients a through d depend on the type of the AO. They are reproduced in table S1 of the supplementary information.

Thus, the total cross section of a molecular target is calculated by adding each partial contribution from the MOs, leading to a weight factor q_k, where the sum index k runs over the occupied MO:

$$\sigma_{\mathrm{DM}}(E) = \sum_{k=1}^{N} 4\pi N_k q_k r_k^2 \left(\frac{R}{E_k} \right)^2 g(u_k).$$
(6)

N_k is the number of electrons occupying the kth MO. This formula comes with two caveats [15]: calculating the molecular weight factors q_k for each MO can be difficult or even impossible, and, the previous expressions for the energy-dependent function g are no longer applicable since they depend on the quantum numbers n and l of the AOs.

Different approaches have been proposed to calculate the q_k weight factors for total cross sections. Bethe first introduced these as functions of the quantum numbers n and l [22], while Margreiter *et al* used a fitting procedure to derive these from experimental data for helium to uranium atoms [14]. Deutsch *et al* expressed each of the MOs by AO contributions of the constituent atoms [23]. This approach is natural if modern quantum chemical software with Gaussian atom-centred basis sets is used for obtaining the MOs from AOs. The orbital radii used in this manuscript were taken from relativistic Dirac–Fock calculations by Desclaux [24].

From the description of the methodologies given above one sees that these contain several approximations which had to be

checked but have proven to be acceptable. In the cases where EICSs have been obtained experimentally, they agree reasonably well with the calculated ones and the experimental accuracy is often in the range of the calculations. EICSs are very difficult to measure and a factor of two or three between published experimental data is not unusual in the literature.

2.3. Quantum mechanical calculations

Density functional theory calculations with the functional B3LYP [25] and the Def2SVP basis-set [26, 27] were performed to obtain the intramolecular bond lengths and the AO coefficients needed for the DM cross-section calculations. The populations needed in the DM scheme are obtained from the MO vectors by correcting for the non-orthogonality of the basis set via the overlap matrix. The kinetic energies of the Hartree–Fock (HF) MOs are used in the BEB formula shown in equation (1).

The MO energies were calculated using electron propagator theory (EPT), with both outer valance Green's function (OVGF) [28] and P3/P3+ [29] propagators and the Def2TVP [27] basis set since this is substantially more accurate than simply taking the MO energies from the HF wave function (Koopmans' theorem).

In all calculations on closed-shell systems the occupation number in equations (1) and (6) is equal to 2 and equal to 1 in open-shell systems. In the latter, α and β orbitals are treated independently, also with respect to their potential and kinetic (for BEB) energy.

Fe and Cr and their diatomic molecules considerer here can be present a variety of spin states. In the solid state the high-spin states have the lowest energy and we found this to hold also for the isolated molecules by calculating their energies for different spin states. In a hot plasma, however, we would expect that not only the high-spin states are present. Therefor we also show the cross sections of all low-spin states (for the neutral molecules). Depending on plasma conditions, the effective cross sections will lie in between. All calculations were performed using the Gaussian 16 software [30].

2.4. Fitting EICS to analytical expressions

The EICSs have been fitted to analytical expressions of the following form:

$$\sigma(E) = \begin{cases} \left(\frac{a_1}{E} \right) \left(1 - \frac{E_{\mathrm{th}}}{E} \right)^{a_2} \left(\ln \left(\frac{E}{E_{\mathrm{th}}} \right) + a_3 + a_4 \left(\frac{E_{\mathrm{th}}}{E} \right) \right), & \text{if } E > E_{\mathrm{th}} \\ 0, & \text{otherwise,} \end{cases}$$
(7)

where σ is expressed in Å^2, E and E_{th} are the kinetic energy of the incident electron and the threshold energy for ionization respectively (both in eV). The coefficients a_1 through a_4 are

fitted so that the expression matches a previously calculated EICS from either the BEB or DM method. They can serve as input for modelling codes that simulate the impurity transport
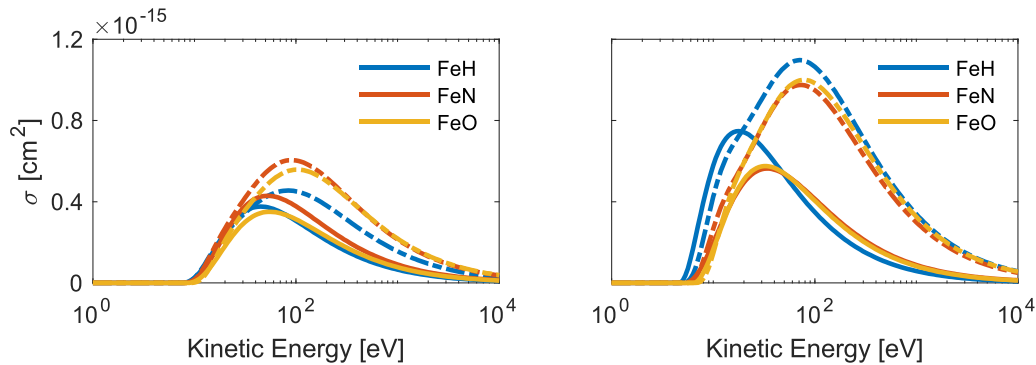
Figure 1. Total electron impact ionization cross sections as function of the kinetic energy of the incident electron for neutral FeH, FeN and FeO molecules from BEB (solid lines) and DM (dashed lines) calculations. The cross sections on the left panel are from the high-spin states and the ones on the right panel from the low-spin states.

in fusion edge plasmas [31] on a macroscopic scale by solving systems of differential equations. An example is the widely used erosion and redeposition (ERO) code [32–34]. Tables S8 and S9 of the supplementary information contain the fitted coefficients. From figures S1 and S2 it can be concluded that equation (7) is in fact suited as a compact representation of the EICSs.

3. Results

3.1. Neutral molecules

As mentioned in the introduction, for analysing the energy balance of a plasma, knowledge of the EICSs of the species present in it is necessary. FeH, FeN and FeO and their chromium counterparts are typical molecules formed by sputtering from steel surfaces by light particles like hydrogen isotopes and then becoming plasmas components themselves. The ionization cross sections for the neutral molecules FeH, FeN and FeO are shown in the left panel of figure 1. With the exception of the high-spin state of FeN, the cross sections obtained with the BEB method are higher than those from the DM formalism. For Cr, the agreement between the DM and BEB results is substantially better for the low-spin molecules (figure 2), while for the high-spin molecules the agreement is about the same for Fe and Cr-based molecules. It makes no appreciable difference if the orbital energies are calculated by the EPT/OVGF or the P3/P3+ method. In figure 1 the former one was used. Their maxima are at similar values of the kinetic energy of the incoming electron but are considerably lower.

There seems to have been no experimental data published for the total cross sections of either of the three iron-based molecules. The predicted first IE of FeO from OVGF calculations on the high-spin state is 8.36 eV (from both OVGF and P3/P3+) and 8.06 eV from Koopmans' theorem, which are close to the experimental gas-phase values of 8.9 eV [35] and 8.71 eV [36]. It is known that the electronic state of FeO is very difficult to describe correctly [37]. The IE thresholds of FeH and FeN, from our EPT calculations, are 6.97 and 7.60 eV respectively.

No experimental data on the total cross sections for the three chromium-containing compounds was found in the

literature. The experimental IE of CrO in the gas-phase ranges from 7.7 to 8.4 eV [35, 38–40], while our prediction from OVGF calculations is 7.72, and 7.50 eV from Koopmans' theorem. The IEs predicted from OVGF calculations on CrH and CrN are 7.01 and 6.30 eV, respectively.

For neutral hydrides and nitrides, the low spin configuration is a doublet, whereas it is a singlet for the oxides. The AO occupancies of the high spin states are given in table S2 for the Fe-based dimers, and in table S3 for the Cr-based ones. Table S4 shows the AO occupancies of the neutral Fe and Cr-based dimers in the low-spin states.

In two former works by Huber *et al* on Be- and W-based molecules [41, 42], similar discrepancies between both methods were observed. These authors also calculated the cross sections of FeO and FeH (high-spin states only), albeit with an effective core potential and valence-only basis set which, overall (and lacking experimental data) should be of similar quality as the one used here. It is only for the sake of consistency that we nevertheless repeated the EICS calculations for these two systems in the high-spin state with the methods used for all other EICSs presented here. Comparing the cross sections from the independent works (figure 3) it can be seen that the differences between the basis sets are smaller than the ones between DM and BEB calculations and that for the latter these differences are smaller than for the DM method.

Similar differences between DM and BEB calculations were noted by Blanco *et al* for bare Be and W atoms [43] and by Huber *et al* for cisplatin [44], a molecule commonly used in chemotherapy. It should be mentioned that also partial electron-impact cross sections can be derived with a semi-empirical treatment [31]. Previous works on a variety of molecules have shown that experimental cross-section values often lie in between those from the DM and BEB methods.

3.2. Cross-sections of cationic species

Electron impact as well as ionization by photons generates cationic states which in turn can be further ionized. The magnitude of the cross sections for iron hydrides, oxides and nitrates is noticeably smaller than the one from the neutral species (figure 1). In the neutral molecules, the BEB cross sections
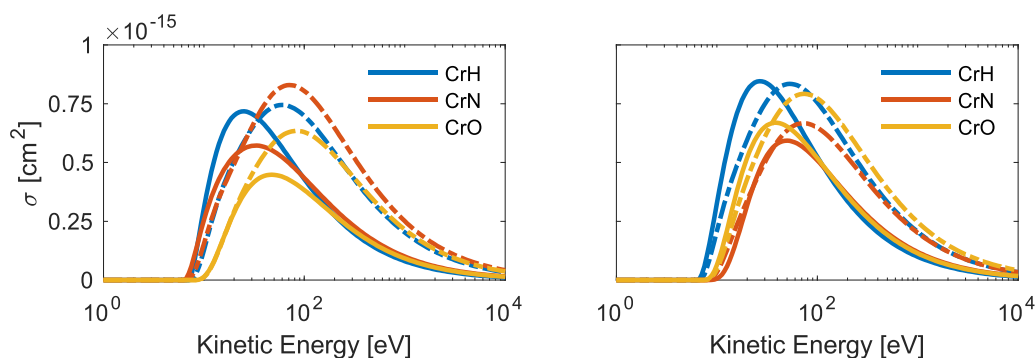
Figure 2. Total electron impact ionization cross sections as function of the kinetic energy of the incident electron for neutral CrH, CrN and CrO molecules from BEB (solid lines) and DM (dashed lines) calculations. The cross sections on the left panel are from the high-spin states while the right panel corresponds to the low-spin states.
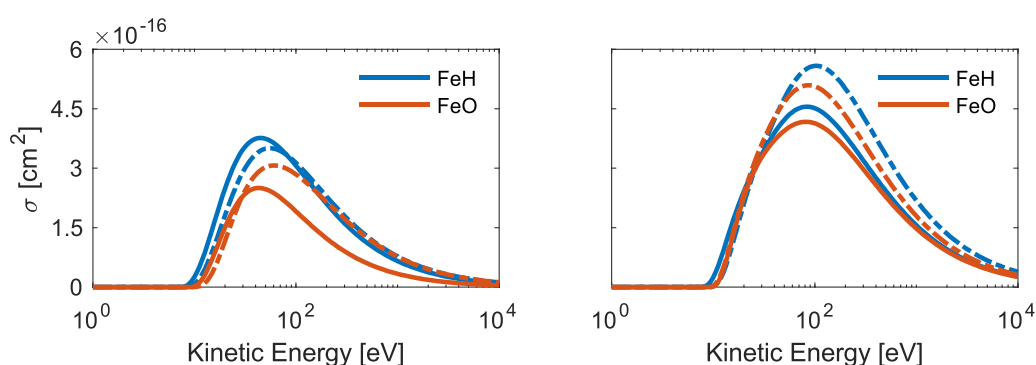
Figure 3. EICSs from DM (left panel) and BEB (right panel) calculations, comparing our cross sections (solid lines) from the all-electron basis set Def2SVP, to the ones using an effective-core potential basis set (Huber *et al* [41, 42]; dashed lines).
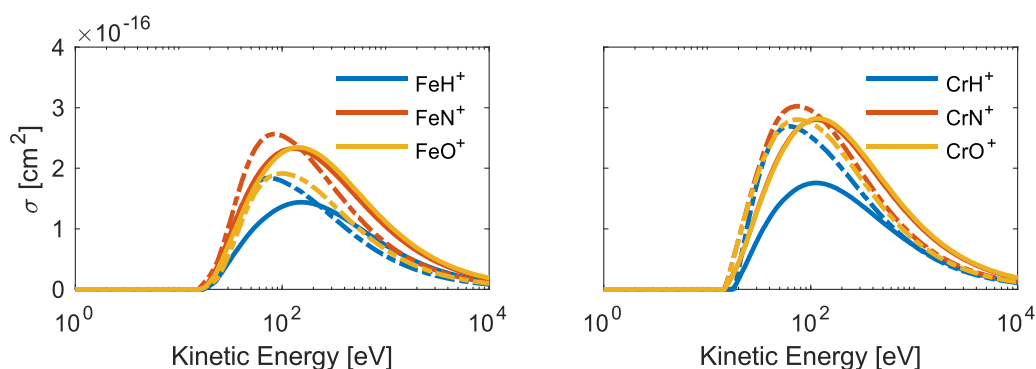
Figure 4. Total cross sections as function of the kinetic energy of the incident electron for the diatomic cations with Fe (left) and Cr (right) using the BEB (solid lines) and DM (dashed lines) methods. All cross sections use OVGF orbital energies.

are mostly lower than those calculated with the DM formalism and this is now the case for all species. As one would expect, the cationic molecules give raise to noticeable smaller EICSs than their neutral counterparts. For the cations only the high-spin states have been considered which are the most stable ones in all cases.

The same observations made for Fe cations hold in general for the Cr-based ones (right panel of figure 4). The EICSs of the Fe and Cr-based diatomic cations are narrower than their neutral counterparts and vanish below 10 eV and above 10^4 eV (figure 4), whereas for the neutral molecules (figures 1 and 2) they are still visible outside this range. For the low-energy part

this is due to the higher first IE of the cations and while for the high energy part it is again a consequence of the more compact cationic MOs with higher kinetic energies. The orbital populations of the cations are given in table S2 (Fe-based dimers) and table S3 (Cr-based dimers) of the supplementary information.

Previous works on a variety of molecules have shown that experimental cross-section values often lie in between those from the DM and BEB methods. In a study by Huber *et al* on Be- and W-based molecules, similar discrepancies between both methods were observed. There, a semi-empirical formula was employed to also derive the partial cross sections [31]. Similar results were noted by Blanco *et al* on bare Be

and W atoms [43]. Differences in the same order of magnitude between the BEB and the DM formalism are reported by Huber *et al* for cisplatin [44], a molecule commonly used in chemotherapy.

4. Conclusions

The EICSs of iron–and chromium monohydride, –oxide and –nitride have been calculated in the energy range of up to 10^4 eV using the BEB and the DM methods for their low-spin and high-spin states. Both methods agree qualitatively well to the shape of the cross-sections but differ up to 40% regarding their magnitudes. This result is in line with former investigations we have performed for other fusion-relevant diatomic molecular species, both metallic and otherwise [31, 44].

The EICSs of the corresponding cations states were also calculated. The deviation between BEB and DM cross sections of the cations is smaller than in case of the neutrals. The calculation of electron production rates. If composition and temperature of a plasma are known, these and other cross sections can be used to get the electron production rate by folding them with the relevant temperature distribution. As such, we believe the present work to be of interest. We plan to extend this study to calculate electron impact excitation cross sections and partial cross sections of key selected molecular targets.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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