Electron-Impact Ionization Cross Sections of Molecules and Ions in Fusion Plasma

Michael Probst, Ivan Sukuba, Jan Urban, Alexander Kaiser, Thana Maihom, Jumras Limtrakul, Kersti Hermansson, Dmitriy Borodin and Stefan E. Huber

1 Institute of Ion Physics and Applied Physics, University of Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria
2 Department of Nuclear Physics and Biophysics, Comenius University, 84248 Bratislava, Slovakia
3 Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen Campus, Nakhon Pathom 73140 and Center for Advanced Studies in Nanotechnology and Its Applications in Chemical, Food and Agricultural Industries, Kasetsart University, Bangkok 10900, Thailand
4 Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand
5 Department of Chemistry - Ångström Laboratory, University of Uppsala, S-75121, Uppsala, Sweden
6 Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Plasmaphysik, 52425 Jülich Germany

E-mail contact of main authors: michael.probst@uibk.ac.at and s.huber@uibk.ac.at

Abstract. We report calculated electron-impact ionization cross sections (EICSs) for the molecules BeHx with x=0-3 and their cations. We apply and compare the Deutsch-Märk (DM) and the binary-encounter-Bethe (BEB) methods. The BEB cross sections are generally smaller than the DM ones. This difference between the two methods is pronounced in the case of the cations, for which the BEB cross sections account for about 50% of the DM cross sections in the cases of largest differences. Lacking experimental data, one can assume that the true cross sections lie between the BEB and DM values.

1. Introduction

Electron-impact cross sections yield the probability of an electron reacting with a particle – a molecule, an ion or an atom – to form a certain reaction product (e.g. a cation) as a function of the energy of that electron. At low energies so-called dissociative electron attachment (DEA) is the predominant reaction mechanism. At energies of the incoming electron higher than the ionization threshold of the particle, a reaction similar to photoionization can occur which causes the particle to lose one of its electrons. In the case of molecules, at high enough energies also further dissociation of the molecular cation can be induced. For the remainder of this work, we focus on electron energies above the ionization threshold, hence omitting DEA, and on particles consisting of chemical elements envisaged in to be present in fusion plasma. In particular, beryllium (Be) is envisaged as a first-wall material in the International Thermonuclear Experimental Reactor (ITER) [1]. Direct exposition of this wall material to plasma components [2] will result in erosion due to the impact of hot plasma containing hydrogen and its isotopes leading to the ejection of Be and its hydrides into the plasma [3-5].

Knowledge of the electron-impact ionization cross sections (EICSs) for components occurring in plasma is important for knowing the energy balance in the plasma which is influenced by the ionization of plasma components by plasma electrons. For example, the electron impact process can remove fast electrons and supply slow ones. It also leads to an abundance of cationic species
that can, possibly at other locations, re-neutralize or become higher charged cations. Generation of neutral and ionized atoms and molecules due to plasma-wall interaction processes may thus profoundly disturb the fusion plasma and also lead to unfavorable re-deposition of materials and composites in other areas of the vessel [6-9].

During the past decades, a number of semi-empirical methods that use quantum-chemically calculated electronic structure information have been developed in order to derive absolute EICSs for various molecules. Their accuracy is usually in the same range as the one of experimental data. Among those, the most-widely used methods are the binary-encounter-Bethe (BEB) theory of Kim et al. [10, 11] and the Deutsch-Märk (DM) formalism [12]. These methods have been successfully applied to atoms, molecules, clusters, ions and radicals [13].

The BEB method is a physical model with few parameters while the DM method strives to obtain accuracy by casting atomic experimental data into a physically sound, semi-empirical expression suitable for extrapolation. Especially, the comparison of results obtained with these two methods based on different assumptions can serve as an advantage for elucidating the dependence of the EICSs on different physical properties of the underlying molecules [14]. This is especially important since EICS are difficult to measure and indeed for most of the interesting species still no measurements exist.

The BEB and DM methods have their limitations, though. They sum over molecular orbital contributions and do not explicitly take into account the geometry of those orbitals. This causes their accuracy to deteriorate for large molecules where molecular orbitals can be shielded from an incoming electron by other orbitals. To remedy this, for example, spatially localized versions of both approaches could be developed. For a fusion plasma this deficiency is not an issue because there only atoms, ions and rather small molecules are present [5].

In foregoing studies, we applied the BEB and DM methods in the context of nuclear fusion research to obtain EICSs of beryllium and its hydrides [15], beryllium-tungsten clusters [16], tungsten and its oxides [17] and iron hydrogen clusters [14]. In the work on beryllium tungsten clusters [16] mentioned above, we explored the effect of molecular geometry (due to the existence of various isomers for a given cluster size) and of the electronic spin configuration on the respective cross sections. We found that while molecular geometry does not significantly affect the resulting cross section, differences in electronic spin configuration can give rise to substantial different cross sections. They can differ by up to 83% in magnitude in the region of the cross section maxima.

In this contribution, we turn our attention once again to EICSs of beryllium and its hydrides. Whereas the molecules covered here had already mostly been studied in their neutral state in Ref. [15], we explore the EICSs of beryllium hydride cations and discuss the influence of the charge state on the resulting cross sections in this work. In particular, we provide EICSs obtained by the BEB and DM methods for the molecular (and atomic) species BeH\textsubscript{x} with x = 0-3 and their singly charged cations. Moreover, we report fit parameters for those cross sections, which are obtained by fitting the calculated data to a fitting expression commonly used in modeling of impurity transport of fusion edge plasmas such as in the ERO code [18-20]. Finally, we discuss how these total cross sections can be used to derive estimates of partial cross sections for individual fragmentation channels for reactions of the kind
\[ e^- + AB \rightarrow A^+ + B + 2e^-, \]
where AB denotes a certain molecule, and A and B are molecular fragments.

2. Methods

2.1. The DM formalism

The DM formalism was originally developed as an easy-to-use semi-empirical approach for the calculation of EICSs of atoms in their electronic ground-state from threshold to about 100 eV.
[12]. In its most recent variant [13, 21], the total single electron-impact ionization cross section \( \sigma \) of an atom is expressed as:

\[
\sigma_{DM}(u) = \sum_{n,l} g_{nl} r_{nl}^2 \xi_{nl} b_{nl}^{(q)}(u) \ln(c_{nl} u) / u,
\]

(1)

where \( r_{nl} \) is the radius of maximum radial density of the atomic sub-shell characterized by quantum numbers \( n \) and \( l \) (as listed in column 1 in the tables of Desclaux [22]) and \( \xi_{nl} \) is the number of electrons in that sub-shell. The sum extends over all atomic sub-shells labeled by \( n \) and \( l \). The \( g_{nl} \) are weighting factors, which were originally determined by a fitting procedure [23, 24] using reliable experimental cross section data for a few selected atoms, for which the accuracy of the reported rate is in the range of 7-15%. The reduced energy \( u \) is given by \( u = E / E_{nl} \), where \( E \) refers to the incident energy of the electrons and \( E_{nl} \) denotes the ionization energy of the sub-shell characterized by \( n \) and \( l \). The energy-dependent quantities \( b_{nl}^{(q)}(u) \) were introduced in an effort to merge the high-energy region of the ionization cross section, which follows the Born-Bethe approximation [25], with the DM formula of the cross sections in the regime of low impact energies. The function \( b_{nl}^{(q)} \) in Eq. (1) has the explicit form:

\[
b_{nl}^{(q)} = \frac{A_1 - A_2}{1 + (u/A_2)^p} + A_2,
\]

(2)

where the four constants \( A_1, A_2, A_3 \) and \( p \) were determined, together with \( c_{nl} \), from reliably measured cross sections for the various values of \( n \) and \( l \). The superscript \( q \) refers to the number of electrons in the \( (n, l) \)-th sub-shell and allows the possibility to use slightly different functions \( b_{nl}^{(q)} \) depending on the number of electrons in the respective sub-shell. At high impact energies \( u \) goes to infinity, the first term in Eq. (2) goes to zero and \( b_{nl}^{(q)}(u) \) becomes a constant ensuring the high-energy behavior predicted by the Born-Bethe theory [25].

The DM formalism has been extended to the calculation of EICSs of atoms in excited states, molecules and free radicals, atomic and molecular ions, and clusters [13]. For the calculation of the EICS of a molecule, a population analysis [26, 27] must be carried out to obtain the weights with which the atomic orbitals of the constituent atoms contribute to each occupied molecular orbital. These weights are obtained from the molecular orbital coefficients after a transformation employing the overlap matrix in order to correct for the non-orthogonality of the atomic basis functions.

2.2. The BEB method

The BEB model [11] was derived from the binary-encounter-dipole model [10] by replacing the \( df/dE \) term for the continuum dipole oscillator strengths by a simpler form. Thus, a modified form of the Mott cross section together with the asymptotic form of the Bethe theory describing the electron-impact ionization of an atom was combined into an expression for the cross section of each molecular orbital:

\[
\sigma(t) = \frac{S}{t + u + 1} \left[ \ln(t) - \frac{1}{2} \left( 1 - \frac{1}{t^2} \right) + 1 + \frac{1}{t} - \ln(t) \right],
\]

(3)

where \( t = T / B, u = U / B, S = 4 \pi a_0^3 NR^2 / B^2, a_0 \) denotes the Bohr radius (0.5292 Å), \( R \) is the Rydberg energy (13.6057 eV), and \( T \) denotes the incident electron energy. \( N, B \) and \( U \) are the electron occupation number, the binding energy (ionization energy), and the average kinetic energy of the respective molecular orbital, respectively. In the BEB model, the total cross section, similarly to the DM method, is then obtained by summation over the cross sections for all molecular orbitals.

The cross section formula given by Eq. (3) has experienced several modifications over the years for atoms and molecules involving orbitals corresponding to principal quantum numbers larger than two [28-33]. The BEB cross section including this modification, which became known also as “acceleration correction” [34] reads:
\[ \sigma_{BEB}(t) = \frac{S}{t + (u+1)/n} \left[ \frac{\ln(t)}{2} \left( 1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \ln(t) \right], \]  

where for atoms \( n = pqn \), with \( pqn \) denoting the principle quantum number, for orbitals with \( pqn \geq 3 \), \( n = 1 \) for orbitals with \( pqn = 1, 2 \), and for molecules \( n = pqn \) if the Mulliken population analysis of the respective molecular orbital yields that the component of a specific atomic orbital with \( pqn \geq 3 \) is dominant, i.e. its contribution is larger than 50%, \( n = 2 \) for singly charged molecular ions, and \( n = 1 \) otherwise.

### 2.3. Quantum chemical calculations

The molecular geometries of the BeH\(_x\), \( x = 1, 2, 3 \), molecules and their respective cations were optimized using the QCISD method [35] in conjunction with the aug-cc-pVTZ basis set [36]. Occupation, binding energy and average kinetic energy for each molecular orbital as required for the calculation of the BEB cross sections (see section 2.2.) were calculated at the HF/aug-cc-pVTZ level of theory. The orbital populations required for the DM formalism were derived from HF calculations in conjunction with the minimal CEP-4G basis set [37-39]. Orbital energies for the outermost valence electrons were calculated with the OVGF method [40] and the aug-cc-pVTZ basis set. The Gibbs free reaction energies reported in Section 3.2 and used for the estimation of partial ionization cross sections were obtained using the G4 extrapolation scheme developed by Curtiss and coworkers [41] which yields an absolute average deviation from experiment of 0.83 kcal/mol for the 454 experimental energies compiled in the G3/05 test set [42].

All calculations were performed with the Gaussian 09 software [43].

### 2.4. Analytical expression of the EICSs

We fitted the cross sections to an expression that resembles the one used in the ERO code [18-20] which is used for impurity transport simulations in fusion edge plasmas. The fitting expression is given by:

\[ \sigma(E) = \left( \frac{a_1}{E} \right) \left[ 1 - \frac{E}{E_t} \right] a_2 \ln \left( \frac{E}{E_t} \right) + a_3 + a_4 \left( \frac{E}{E_t} \right). \]  

Here, the cross section \( \sigma \) is expressed in \( 10^{-16} \) cm\(^2\), the incident electron energy \( E \) and the threshold energy (first ionization energy) \( E_t \) are both expressed in eV, and the fit parameter \( a_1 \) is expressed in \( 10^{-16} \) cm\(^2\) eV. The fit parameters \( a_2, a_3 \) and \( a_4 \) are dimensionless.

### 3. Results

#### 3.1. EICSs of BeH\(_x\)\(^+\), \( x=0-3 \)

The EICSs obtained with the BEB and DM methods for the molecular (and atomic) species BeH\(_x\) and for their cations, i.e. BeH\(_x^+\), with \( x=0-3 \) are depicted in Fig. 1(a). The cross sections for Be, BeH and BeH\(_2\) were already reported and discussed in a previous work [15] and are repeated here for allowing comparison with the EICSs of their cations. Details concerning the EICSs of Be, BeH and BeH\(_2\) can be found in Ref. [15]. Fits obtained using Eq. (5) are shown also in Fig. 1(a) (solid lines). The various fit parameters are supplied in Table 1. In Fig. 1(b), the optimized geometries of BeH\(_x\) with \( x = 1,2,3 \) and their cations are depicted. For both methods, the EICSs for the cations are substantially smaller (within factors of 2-6) than the respective cross sections for the neutral systems, see also Table 1. This can be expected since
TABLE I: IONIZATION THRESHOLDS, $E_{th}$ IN eV, CROSS SECTION MAXIMA IN $10^{-16}$ cm$^2$, AND THEIR RESPECTIVE ENERGIES IN eV, TOGETHER WITH THE FIT PARAMETERS OBTAINED BY FITTING THE CROSS SECTIONS TO EQ. (5). THE UNIT OF $a_1$ IS $10^{-16}$ cm$^2$ eV, WHILE $a_2$, $a_3$ AND $a_4$ ARE DIMENSIONLESS.

<table>
<thead>
<tr>
<th>Method</th>
<th>Species</th>
<th>$E_{th}$</th>
<th>$\sigma_{max}$</th>
<th>$E_{max}$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEB</td>
<td>Be</td>
<td>8.42</td>
<td>3.15</td>
<td>39.5</td>
<td>121.80</td>
<td>1.4010</td>
<td>-0.24820</td>
<td>0.64830</td>
</tr>
<tr>
<td></td>
<td>BeH</td>
<td>8.47</td>
<td>2.97</td>
<td>48.5</td>
<td>131.10</td>
<td>2.1430</td>
<td>-0.19960</td>
<td>0.67930</td>
</tr>
<tr>
<td></td>
<td>BeH$_2$</td>
<td>12.20</td>
<td>2.93</td>
<td>57</td>
<td>154.90</td>
<td>1.5410</td>
<td>-0.09588</td>
<td>0.57570</td>
</tr>
<tr>
<td></td>
<td>BeH$_3$</td>
<td>9.97</td>
<td>3.59</td>
<td>56.5</td>
<td>177.50</td>
<td>2.3680</td>
<td>-0.04531</td>
<td>0.70580</td>
</tr>
<tr>
<td></td>
<td>Be$^+$</td>
<td>18.13</td>
<td>0.44</td>
<td>67.5</td>
<td>31.26</td>
<td>0.4839</td>
<td>-0.28980</td>
<td>0.32330</td>
</tr>
<tr>
<td></td>
<td>BeH$^+$</td>
<td>20.36</td>
<td>0.72</td>
<td>74.5</td>
<td>48.31</td>
<td>0.9539</td>
<td>0.16620</td>
<td>0.13540</td>
</tr>
<tr>
<td></td>
<td>BeH$_2^+$</td>
<td>19.91</td>
<td>1.01</td>
<td>76.5</td>
<td>66.01</td>
<td>1.0820</td>
<td>0.27740</td>
<td>-0.01277</td>
</tr>
<tr>
<td></td>
<td>BeH$_3^+$</td>
<td>19.45</td>
<td>1.18</td>
<td>81</td>
<td>79.00</td>
<td>1.3690</td>
<td>0.32820</td>
<td>0.00140</td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>9.32</td>
<td>3.96</td>
<td>31</td>
<td>74.84</td>
<td>1.156</td>
<td>1.4910</td>
<td>-0.6679</td>
</tr>
<tr>
<td></td>
<td>BeH</td>
<td>8.36</td>
<td>4.06</td>
<td>43.5</td>
<td>95.26</td>
<td>2.772</td>
<td>1.8180</td>
<td>-0.5225</td>
</tr>
<tr>
<td></td>
<td>BeH$_2$</td>
<td>12.11</td>
<td>4.69</td>
<td>50.5</td>
<td>141.60</td>
<td>1.812</td>
<td>1.4370</td>
<td>-0.4379</td>
</tr>
<tr>
<td></td>
<td>BeH$_3$</td>
<td>9.57</td>
<td>6.05</td>
<td>52</td>
<td>159.10</td>
<td>3.096</td>
<td>2.1220</td>
<td>-0.5094</td>
</tr>
<tr>
<td></td>
<td>Be$^+$</td>
<td>18.14</td>
<td>0.61</td>
<td>60.5</td>
<td>22.95</td>
<td>1.121</td>
<td>1.3940</td>
<td>-0.6407</td>
</tr>
<tr>
<td></td>
<td>BeH$^+$</td>
<td>20.43</td>
<td>1.17</td>
<td>79</td>
<td>61.91</td>
<td>1.391</td>
<td>0.9863</td>
<td>-0.3153</td>
</tr>
<tr>
<td></td>
<td>BeH$_2^+$</td>
<td>19.24</td>
<td>1.91</td>
<td>81</td>
<td>97.86</td>
<td>1.730</td>
<td>1.1700</td>
<td>-0.3380</td>
</tr>
<tr>
<td></td>
<td>BeH$_3^+$</td>
<td>19.47</td>
<td>2.46</td>
<td>88.5</td>
<td>125.20</td>
<td>2.134</td>
<td>1.5750</td>
<td>-0.6233</td>
</tr>
</tbody>
</table>

after removal of one electron, the remaining ones are more tightly bound to the nuclei, which is also reflected in the energy required to remove a further electron, i.e. the ionization energies of the cations listed also in Table 1 (denoted there as $E_{th}$). Also the cross section maxima are shifted accordingly to higher energies for the cations, compared to the neutral systems.

The energies at which the cross sections become maximal, see also Table 1, agree well within 10 eV between the two methods. The BEB cross sections are generally smaller than the DM cross sections which is more pronounced in the case of the cations than in the case of the neutral species. For the neutral species, the largest difference is found for BeH$_3$, for which the BEB cross section is about 60% of the DM cross section at the maximum. In case of the cations, the differences grow continuously with the size of the considered molecules. Whereas the BEB cross section amounts to about 70% of the DM cross section in the case of atomic Be$^+$, the BEB cross section is only about half of the DM cross section in the case of BeH$_3^+$. It must be kept in mind, however, that discrepancies between the results of different calculations, as well as similarly large discrepancies between calculated and experimentally determined cross sections are not unusual [11, 13, 24]. It can also be seen from Fig. 1(a) that Eq. (5) gives an excellent fit to all cross section data. The obtained fit parameters are summarized in Table 1.

4. Conclusions

We applied the Deutsch-Märk (DM) and the binary-encounter-Bethe (BEB) methods to calculate total electron-impact ionization cross sections (EICSs) for the species BeH$_x$ with $x = 0-3$ and their cations. The EICSs for most neutral systems were already discussed in earlier work and were included in this work for the purpose of comparison with their cationic counterparts. New data is supplied also for BeH$_3$ for which the DM cross section maximum is
FIG. 1.  
(A): BEB (LEFT PANELS) AND DM (RIGHT PANELS) EICSS OF BeHₓ WITH x=03 (UPPER PANELS) AND THEIR CATIONS (LOWER PANELS). FITS OBTAINED USING EQ. (5) ARE SHOWN ALSO (SOLID LINES).

(B): OPTIMIZED GEOMETRIES OF THE CONSIDERED BeHₓ MOLECULES AND THEIR CATIONS TOGETHER WITH SOME OF THEIR STRUCTURAL PARAMETERS (BOND LENGTHS ARE GIVEN IN Å AND ANGLES IN DEGREES).

6.05 × 10⁻¹⁶ cm². The DM cross section maxima in the case of the cationic systems are 0.61, 1.17, 1.91 and 2.46 × 10⁻¹⁶ cm² for Be⁺, BeH⁺, BeH₂⁺ and BeH₃⁺, respectively. The BEB cross sections are generally smaller than the DM ones. In case of the cations, the BEB cross sections account for about 50% of the DM cross sections in the cases of largest differences between the two methods. Experimental data are in much need but lacking them, one can assume from the experience gained with other species that the true cross sections lie between the BEB and DM values.

Acknowledgments

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014–2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission. It was also supported by the Austrian Ministry of Science BMWF as part of the UniInfrastrukturprogramm of the Focal Point Scientific Computing at the University of Innsbruck. The computational results presented have been achieved in part using the HPC infrastructure LEO of the University of Innsbruck.
References


