Reactive collisions involving the BeH molecular system

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Abstract. In the divertor and fusion edge plasma regions reactive collisions involving the BeH molecular system are taking place. Theoretical ab initio quantum studies of electron collisions with BeH$^+$ resulting in either dissociative recombination, vibrational excitation or dissociative excitation are performed for ions in different vibrational states as well for different isotopologues. Furthermore, the mutual neutralization reaction in collisions of H$^-$ with Be$^+$ is studied semiclassically.

1. Introduction
At the ITER fusion reactor in France, there are plans for having beryllium on the primary walls [1]. The Be will enter the plasma and Be-containing atomic and molecular ions will be formed in the cooler divertor region of the fusion reactor. Within a coordinated research project initiated by IAEA (International Atomic Energy Agency) with the title “Light Element Atom, Molecule and Radical Behavior in the Divertor and Edge Plasma Regions” [2] we have performed theoretical studies of collisional processes involving the BeH molecular system. In electron collisions with the BeH$^+$ molecular ion a neutral resonant state is formed. If the system dissociates into neutral fragments the process is dissociative recombination (DR) [3]. The system can also autoionize (re-emit the electron). If a bound vibrational state of the ion is formed the reaction results in vibrational excitation (or de-excitation) (VE), while if the system autoionizes into a state above the dissociation limit of the ion, the process is called resonant dissociative excitation (DE). These processes have here been studied ab initio and using a quantum mechanical description. Furthermore, the possible presence of the H$^-$ anion in the fusion plasma [4, 5] motivated studies of the mutual neutralization process taking place when H$^-$ collides with Be$^+$. This study has been carried out using a semi-classical model. The collisional processes in the divertor plasma occur at relative low energies (1 meV to 50 eV). Furthermore, the molecular ions present in the plasma may be vibrationally excited. Different isotopologues of the ions are present. We study the effect of vibration as well as isotopic substitution on the above mentioned reactive collisional processes. State specific cross sections as well as final state distributions for these reactions are presented.
2. Theory

2.1. Calculation of relevant electronic states

In processes such as dissociative recombination, vibrational or dissociative excitation, the electronic molecular states involved are often electronic resonant states. The potential energy curves of the resonant states are situated above the ground state potential of the ion. These states interact with the ionization continuum and the interaction give rise to the autoionization width and the finite lifetime of the state. To compute electronic resonant states, electron scattering calculations are employed. We use the complex-Kohn variational method [6] to obtain the energy positions and autoionization widths of the resonant states. The electron scattering calculations are combined with consistent structure calculations of bound electronic states. For BeH, we used [3] the multi-reference configuration interaction method with a reference space consisting all excitations of the electrons among the seven lowest molecular orbitals and additional single external excitations.

The electronic states are “quasi-diabatized” [3]. The diabatization is based on the assumption that the configurations of the resonant electronic states can be followed as the internuclear distance changes. The Rydberg states converging to the ground state of BeH$^+$ as well as the ionization continuum, all have dominant configurations of the form $(1\sigma)^2(2\sigma)^2(n\lambda)^1$, where $n\lambda$ is a more or less diffuse orbital. The configurations of the resonant states are different from this and by following the configurations of the resonant states as the internuclear distance changes, an initial approximation for the quasidiabatic states can be obtained. To compute the electronic couplings, the adiabatic states are transformed using an orthogonal transformation matrix that is constructed by successive two-by-two rotations. The transformation matrix has a number of parameters that are optimized by fitting the diagonal terms of the potential energy matrix to the guessed quasidiabatic potential energy curves. In Fig. 1 the quasidiabatic potential energy curves of BeH are displayed together with the ground state potential of the ion.

The potential energy curves are computed for internuclear distances smaller than 10 a$_0$. The ion-pair state associated with the Be$^+$+H$^-$ limit asymptotically has $^2\Sigma^+$ symmetry. In this study we did not compute the electronic states involved in the avoided crossings occurring at larger distances when the ion-pair state interacts with the covalent states associated with Be$^*$+H limits.

2.2. Nuclear dynamics

In electron recombination processes the nuclear dynamics on coupled electronic states are described using wave packet propagation by a direct integration of the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi = \left(-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + U^d\right)\Psi, \tag{1}$$

When several coupled states are involved $U^d$ is the diabatic non-diagonal potential energy matrix. Autoionization from resonant states is included using the local approximation [7]. The potential energy curves of the resonant states are given by

$$U^d_{ii}(R) = V_i(R) - i\frac{1}{2}\Gamma_i(R), \tag{2}$$

where $\Gamma_i(R)$ is the autoionization width of the resonant state. The electron recombination with the molecular ion is described using the initial condition for the wave packets

$$\Psi_i(R, t = 0) = \sqrt{\frac{\Gamma_i(R)}{2\pi}}\chi_v(R), \tag{3}$$

where $\chi_v(R)$ is the initial wave function of the ion. Thus, in the present study, only the electronic couplings between the ionization continuum and the resonant states are included and...
the direct capture into the Rydberg states by non-adiabatic couplings is not considered. This indirect pathway to dissociative recombination and vibrational excitation has recently [8] been incorporated for the \( e^- - \text{BeH}^+ \) scattering processes using multi-channel quantum defect theory.

The cross section of dissociative recombination is computed [7, 9] by projecting the asymptotic wave packet onto energy-normalized eigenstates of the fragments

\[
\sigma_i (R) = \frac{2\pi^3}{E} g \left| \langle \Phi_i^E (R) | \Psi_i (t_{\infty}, R) \rangle \right|^2.
\] (4)

Here \( g \) is the ratio of multiplicity between the final and initial states and the total DR cross section is obtained by summing the contributions from all states.

The cross section for vibrational excitation is obtained by computing the transition matrix element from each resonant states [7, 10]

\[
T_{v'v}^i (E) = -i \int_0^\infty e^{iEt} \left\langle \chi_{v'} (R) | \sqrt{\frac{\Gamma_i (R)}{2\pi}} | \Psi_i (t, R) \right\rangle dt.
\] (5)

The total transition matrix is obtained from a coherent sum of the T-matrix elements for all resonant states of the same symmetry

\[
\sigma_{v'v} (E) = \frac{2\pi^3}{E} \left| \sum_i T_{v'v}^i (E) \right|^2.
\] (6)
Table 1. Parameters used in the Landau-Zener study of mutual neutralization in Be$^+$ + H$^-$ collisions.

| Asymptotic limit | Binding energy (eV) | $R_e$ (a$_0$) | Coupling strength (eV) |
|------------------|---------------------|---------------|------------------------|
| H + Be$^+$       | 0                   |               |                        |
| H$^+$ + Be$^+$   | 0.7542              |               |                        |
| H + Be(2s4s $^1S$), H +Be(2s3d $^1D$) | 1.330 | 47.33 | 8.025 $\cdot 10^{-4}$ |
| H + Be(2s3d $^3D$) | 1.629 | 31.22 | 9.252 $\cdot 10^{-3}$ |
| H + Be(2s3p $^1P$) | 1.860 | 24.77 | 2.867 $\cdot 10^{-2}$ |
| H + Be(2s3p $^3P$) | 2.019 | 21.74 | 8.155 $\cdot 10^{-2}$ |
| H + Be(2p$^2$ $^1D$) | 2.270 | 18.27 | 8.189 $\cdot 10^{-2}$ |
| H + Be(2s3s $^1S$) | 2.544 | 15.64 | 1.127 $\cdot 10^{-1}$ |
| H + Be(2s3s $^3S$) | 2.866 | 13.46 | 2.782 $\cdot 10^{-1}$ |
| H + Be(2s2p $^1P$) | 4.045 | 9.358 | 2.820 $\cdot 10^{-1}$ |

When the transition matrix for dissociative excitation is computed, the wave packet is instead projected onto the energy normalized continuum functions of the ground ionic state. The total DE cross section is obtained by integrating over all energetically open continuum functions

$$
\sigma_{DE}(E) = \pi \frac{k^2}{E} \int |T_{ee}|^2 d\epsilon.
$$

(7)

2.3. Semi-classical Landau-Zener study

In order to compute the cross section for mutual neutralization when Be$^+$ collides with H$^-$ a semi-classical Landau-Zener [11, 12] study has been performed. Here the avoided crossings occurring between the ionic and covalent states at large internuclear distances ($R > 9$ a$_0$) are considered. Since the adiabatic potential energy curves of the involved states are not computed \textit{ab initio}, semi-classical expressions of quasidiabatic potential energy curves and couplings are applied. At large internuclear distances, the ion-pair state is assumed to have a potential of the form

$$
U_{ip}(R) = U_{th} - \frac{1}{R} - \frac{\alpha}{2R^4},
$$

(8)

where $U_{th}$ is the asymptotic threshold energy and $\alpha$ is the polarizability of H$^-$ [13]. The diabatic covalent states are assumed to have potential energy curves with constant energies (independent on $R$). The electronic couplings between the ionic and covalent states are computed using the approach developed by R K Janev based on an one-electron approximation [14, 15, 16]. The parameters of the potentials and couplings are summarized in Table 1. When two curve crossings occur close to each other, an effective state is used where the energy and crossing point are obtained by the average of those involved and the coupling strength is given by the roots of the sums of the squares of the corresponding coupling elements [16].

By applying the semi-classical Landau-Zener model described by Bates and Lewis [17], the cross section for mutual neutralization is given by

$$
\sigma(E) = \frac{\pi}{k_i^2} \sum_{\ell} (2\ell + 1) P_{\ell}(E).
$$

(9)

Here, $k_i$ is the wave number of the reactants and $P_{\ell}(E)$ is the multi-state Landau-Zener probability that the reacting ion-pair forms neutral fragments after passing through the crossings between ionic and covalent states both on the way in and out. This probability depends on the angular quantum number $\ell$ of the system since the centrifugal barrier $\ell(\ell+1)/2\mu R^2$ will be added
Figure 2. Total cross section for the direct mechanism of dissociative recombination of BeH$^+$ and BeD$^+$ in the $v = 0$ and $v = 1$ vibrational states. Also the cross section computed using uncoupled quasidiabatic potential energy curves for BeH$^+$ ($v = 0$) is displayed.

to the diabatic potentials. For large enough $\ell$, the crossing points $R_x$ at smaller distances might not be reached [17]. When calculating the cross section for mutual neutralization, the contributions from the different pathways must be added together. Here the contributions are added incoherently.

3. Results and Discussion

3.1. Dissociative recombination

The direct dissociative recombination cross section of BeH$^+$ is computed using the wave packet approach described above. The results [3] are summarized in the Fig. 2. The electronic couplings between the neutral states do not significantly change the magnitude of the cross section, but create sharp oscillations that can be interpreted as Feshbach resonances formed when the states open for dissociation are coupled to nuclear bound states [3]. As mentioned above, the indirect mechanism of dissociative recombination, i.e., the direct capture to bound Rydberg states via non-adiabatic couplings and subsequent predissociation is here not included. In a separate study [8] using multi-channel quantum defect theory, both the direct and indirect pathways are considered.

By changing the initial state of the target ion to $v = 1$, the cross section for vibrationally excited ions is computed. Due to the change in the vibrational energy of the target ion, the high energy peak in the cross section is shifted toward smaller energies. Furthermore, the larger capture probability for the vibrationally excited target ion, causes a slightly larger cross section at low energies.

Finally by changing the reduced mass of the system to the one of BeD, the cross section for
DR of BeD$^+$ is computed. The heavier isotopologue has a DR cross section similar to the one of BeH$^+$ both with respect to the magnitude and the overall shape. The high-energy peak is slightly reduced. At the same collision energy, the velocity of the heavier isotopologue is slower, which increases the time in the regions where autoionization can occur. This will increase the probability for autoionization and lower the cross section.

For modeling the fusion plasma of the divertor not only the total cross section is important, but also the final state distribution. It is essential to know what fragments are formed in the reaction. In the present calculation of DR, twelve states of $^2\Sigma$ symmetry, nine states of $^2\Pi$ symmetry and one state of $^2\Delta$ symmetry are included. Asymptotically these are correlated with Be$^*$+H. As mentioned above, the adiabatic states are quasidiabatized and electronic couplings for internuclear distances < 10 a₀ are included. By analyzing the dissociating fluxes on respective electronic states, the final state distributions can be computed. We thus neglect any interactions between the electronic states outside the edge of our grid. We do not consider ionic-covalent couplings occurring at large internuclear distances. (This is reasonable since the $^2\Sigma^+$ electronic states only have minor contributions to the total DR cross section at low energies [3]).

The resulting final state distributions as a function of the collision energy are displayed in Fig. 3. It should be noted that at low energies (< 0.5 eV), dissociation into Be(2s2p $^1P$)+H dominates. The lowest resonant state of $^2\Pi$ symmetry dissociates into this limit and this state dominates the low energy DR. At higher energies, the Be(2p$^2$ $^1D$)+H channel becomes important, which can be understood from the opening of the resonant state of $^2\Delta$ symmetry. At even higher energies, the uncertainties in the computed branching ratios are larger since it becomes harder to identify the asymptotic limits of the excited states.

**Figure 3.** Final state distributions in DR of BeH$^+$. 

[Image of Figure 3: Final state distributions in DR of BeH$^+$.]
3.2. Vibrational excitation
The cross section for vibrational excitation (or de-excitation) $[\text{BeH}^+(v)+e^- \rightarrow \text{BeH}^* \rightarrow \text{BeH}^+(v')+e^-]$ is computed using a model where the couplings between the neutral states are neglected. This is justified from the assumption that autoionization from the resonant state occurs at small distances where the couplings can be neglected. The cross section is computed for initial target ions in $v = 0$ (a) and $v = 1$ (b) and for final states of $v' = 0$, $1$, ..., $4$.

The computed cross sections displayed in Fig. 4 show thresholds at the energies of the opening of respective vibrational channel. The sharp structures in the cross sections are due to resonances due to bound vibrational states. The structures disappear above the dissociation limit of the ion.

3.3. Dissociative excitation
The cross section for resonant dissociative excitation $[\text{BeH}^+(v)+e^- \rightarrow \text{BeH}^* \rightarrow \text{Be}^++\text{H}^++e^-]$ is obtained from the model where electronic couplings between the neutral states are neglected. The cross section is computed for vibrational states of the target ion $v = 0, 1, ..., 5$. As can be seen in Fig. 5 the cross sections are peaked at higher energies (around 3 eV) and increases with increasing vibrational state of the ion. The cross section for DE is dominated by capture into resonant states of $^2\Sigma^+$ symmetry.

3.4. Mutual neutralization
When Be$^+$ collides with H$^-$, the non-adiabatic couplings at large internuclear distances causes electron transfer and formation of neutral fragments, Be$^* + \text{H}$. In the present semi-classical...
Landau-Zener study all electronic couplings at small distances ($R < 9 \, a_0$) are neglected. Furthermore, autoionization from the neutral molecular system is not included. The calculations are performed for reduced masses corresponding to the BeH, BeD and BeT molecular systems. As can be seen in Fig 6, the computed cross sections show an $E^{-1}$ energy dependence with a very small isotope effect. By analyzing the cross sections for each final state, it is found that the low energy mutual neutralization is dominated of formation by $\text{Be}(2s3p \, ^1P) + \text{H} \ [60\%]$ and $\text{Be}(2s3d \, ^3D) + \text{H} \ [40\%]$.

4. Summary
Using a quantum ab initio approach dissociative recombination, resonant vibrational excitation and dissociative excitation of BeH$^+$ have been studied. We have computed total cross sections and final state distributions for these processes. The influences of initial vibrational state of the ion and isotopic substitution have been investigated. Furthermore, using a semi-classical Landau-Zener study we report the cross section for mutual neutralization in collisions of Be$^+$ with different isotopes of H$^-$. These are molecular processes that could play an important role for the modeling of the fusion plasma of the divertor at ITER.

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Figure 6. Total cross section for mutual neutralization in collision of Be$^+$ with H$^-$, D$^-$ and T$^-$. 

Research Project on "Light Element Atom, Molecule and Radical Behaviour in the Divertor and Edge Plasma Regions"

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