Electronic and photonic reactive collisions in edge fusion plasma and interstellar space: Application to H$_2$ and BeH systems

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Abstract. Reactive collisional and radiative elementary processes rate coefficients have been either computed using multichannel-quantum-defect theory methods, or measured in merged-beam (storage ring) and crossed-beam experiments. The reaction mechanisms are explained and output data are displayed in ready-to-be-used form, appropriate for the modeling of the kinetics of the edge fusion plasma and of the interstellar molecular clouds.

1. Introduction
The collision of an electron of energy $\varepsilon$ with a molecular cation initially in its ground electronic state on its ro-vibrational level ($N_i^+, v_i^+$) can cause the formation of various superexcited states,
decaying eventually by autoionization and predissociation to different products:

\[
AB^+(N_i^+, v_i^+) + \epsilon^-(\epsilon) \rightarrow AB^*, AB^{*(c)}, AB^{**}, AB^{***(c)} \rightarrow \begin{cases} 
[A + B]_{(\epsilon)} 
\end{cases} (1a)
\]

\[
AB^+(N_f^+, v_f^+) + \epsilon^- (\epsilon_f) \rightarrow AB^+, AB^{*(c)} \rightarrow \begin{cases} 
[A + B^+]_{(\epsilon)} + \epsilon^-(\epsilon_f) 
\end{cases} (1b)
\]

\[
[A + B^+]_{(\epsilon)} + \epsilon^-(\epsilon_f) \rightarrow \begin{cases} 
(A + B^+)_{(\epsilon)} + \epsilon^-(\epsilon_f) 
\end{cases} (1c)
\]

According to the type of these products, different processes take place: Dissociative Recombination (DR (1a)), Elastic, Inelastic or Superelastic Collisions (EC, IC, SEC (1b)), corresponding to the final energy of the electron \(\epsilon_f\) equal, smaller or larger than \(\epsilon\) respectively, and, if \(\epsilon\) exceeds the dissociation energy of the target cation, electron impact ion dissociation, i.e. Dissociative Excitation (DE (1c))[1, 2, 3, 4, 5]. Here \(AB^*\) stands for bound states from both electronic and vibrational point of view, \(AB^{*(c)}\) for states from the electronic continuum (superscript (c)), \(AB^{**}\) for bound states from the electronic point of view but dissociative (i.e. from the vibrational continuum), \(AB^{***(c)}\) for states from the electronic continuum and dissociative, and \(\epsilon\) for the relative kinetic energy release of the heavy products. Eqs. (1) are appropriate for diatomic systems, but can be generalized for polyatomic ones.

The same superexcited states as those appearing in the common part of eqs. (1) and, consequently, the same products, occur through the photoabsorption by a neutral molecule:

\[
AB(N_i, v_i) + h\nu \rightarrow AB^*, AB^{*(c)}, AB^{**}, AB^{***(c)} \rightarrow \begin{cases} 
[A + B]_{(\epsilon)} 
\end{cases} (2a)
\]

\[
AB^+(N_f^+, v_f^+) + \epsilon^- (\epsilon_f) \rightarrow AB^+, AB^{*(c)} \rightarrow \begin{cases} 
[A + B^+]_{(\epsilon)} + \epsilon^-(\epsilon_f) 
\end{cases} (2b)
\]

\[
[A + B^+]_{(\epsilon)} + \epsilon^- (\epsilon_f) \rightarrow \begin{cases} 
(A + B^+)_{(\epsilon)} + \epsilon^-(\epsilon_f) 
\end{cases} (2c)
\]

resulting in Photodissociation (PhD) (2a), Photoionization (PhI) (2b) [6, 7, 8, 9] and Dissociative Photoionization (DPhI) (2c) [10].

And finally, the dissociative states \(AB^{**}\) are intermediate stages of excitation in the high-energy electron-impact dissociation of molecules [11]:

\[
AB(N_i, v_i) + \epsilon^- (\epsilon) \rightarrow AB^{**} + \epsilon^- (\epsilon_f) \rightarrow [A + B]_{(\epsilon)} + \epsilon^- (\epsilon_f) \ . (3)
\]

All the above processes drive the particle densities in fusion plasmas close to the walls and in the divertor region [12, 13, 14, 15], in various media of astrophysical interest [16, 17, 18, 19], in the hypersonic entry plasmas [20], and in many other environments of fundamental or technological relevance.

The present paper collects the most relevant data - cross sections and rate coefficients - concerning these reactions and available today as output of our studies performed in the frame of the CRP "Light Element Atom, Molecule and Radical Behaviour in the Divertor and Edge Plasma Regions" with IAEA. It is organized as follows: Sections 2, 3 and 4, devoted to the processes - (1), (2), (3) - respectively, have all the same structure, namely after an outline of the relevant theoretical approach and/or the experimental techniques, the cross sections and the rate coefficients are displayed, directly in graphs and, when available, in tables containing the parameters for quick generation by interpolation. Section 5 contains the conclusions and the perspectives.

2. Electron/molecular cation reactive collisions

2.1. The stepwise MQDT-type approach

The dynamics of the infinite series of \(AB^*\) states, often called 'Rydberg resonances', appearing in (1), is elegantly and efficiently modeled by a method [21, 22, 23, 24, 25] based on the Multichannel Quantum Defect Theory (MQDT) [26, 27, 28, 29]. The processes (1) result from the coupling
between ionization and dissociation *channels*, i.e. groups of states characterized by a common set of quantum numbers and by the same fragmentation threshold (either for ionization, or for dissociation), having the energy below or above this threshold. More specifically, within a *quasi-diabatic* representation [22, 23, 30], an *ionization* channel is built starting from the ground electronic state of the ion on one of its ro-vibrational levels $N^+v^+$, and is completed by gathering all the single-electron states of a given orbital quantum number $l$, describing an ‘optical’ electron. These single-electron states describe, with respect to the $N^+v^+$ threshold, either a ‘free’ electron - in which case the total state $AB^{+\ast(c)}$ corresponds to (auto)ionization - or a bound one - in which case the total state $AB^\ast$ corresponds to a temporary capture into a Rydberg state. Meanwhile, a *dissociation* channel relies on an electronically bound state $AB^{\ast\ast}$ whose potential energy in the asymptotic limit is situated below the total energy of the system.

Accordingly, the ionization channels gather together $AB^\ast$ and $AB^{+\ast(c)}$ states, and the dissociation channels correspond to $AB^{\ast\ast}$ states. As for those of $AB^{+\ast(c)}$ type, they can be classified either into dissociation, or into ionization channels, but the latter option has been preferred so far. Given the total energy of the molecular system, a channel is *open* if this energy is higher than the energy of its threshold, and *closed* in the opposite case. In the modeling of the reactions (1)-(3), relying exclusively on the open channels means accounting for the *direct* mechanism only. The inclusion of the closed channels - including $AB^\ast$ states - allows for the *indirect* mechanism, which interferes with the direct one resulting in the *total* process.

In order to illustrate the concept of open and closed channels, and to be more specific, we address the case of the HD$^+$/HD system, for which a relevant energy diagram - restricted to the $1\Sigma_g^+$ symmetry of the neutral - is given in Figure 1. Obviously, the only dissociation channel present here, represented by the HD$^{\ast\ast}$ $1\Sigma_g^+ (2\sigma_2^u)$ state, corresponding to the red curve in this figure, is open, since the asymptotic limit of this curve is situated below the ground vibrational level of the cation. For simplicity, we will assume that a single partial wave of the electron is dominant in the ionization channels. The thick, violet, horizontal lines stand for possible values of the total energy of the system. $E_1$ corresponds to the case where the only open ionization channel is that associated to the ion ground vibrational state ($v^+ = 0$), all the other channels, which are of ionization type, associated to $v^+ = 1, 2, \ldots$ are closed, and correspond to families of states of the type HD$^\ast$. A Born-Oppenheimer - and therefore, *approximate* - picture of some of these states, i.e. those labelled by $1\Sigma_g^+$ $(1s\sigma_g^1 3s\sigma_g)$, $v = 0, 1, 2, \ldots$ is shown in green in Figure 1. $E_2$ represents a total energy for which ionization channels associated to $v^+ = 0 – 7$ are open, and those associated to $v^+ \geq 8$ are closed.

Our MQDT approach starts with the building of the interaction matrix $\Psi$, performed in the ‘A-region’ [31], where the Born-Oppenheimer context is appropriate for the description of the collision system. The good quantum numbers in this region are $N$, $M$, and $\Lambda$, associated respectively to the total angular momentum and its projections on the z-axis of the laboratory-fixed and of the molecule-fixed frames. In the A-region, the states belonging to an ionization channel may be modeled reasonably well with respect to hydrogenic states in terms of the quantum defect $\mu_\Lambda$, which is dependent on the internuclear distance $R$, but assumed to be independent of energy. An ionization channel is coupled to a dissociation one, labeled $d_j$, on electronic level first, through an $R$-dependent scaled ‘Rydberg-valence’ interaction term, $V^{(e)\Lambda}_{d_j,l} \chi_{\Lambda}^A$, which is assumed to be independent of the energy of the electronic states pertaining to the ionization channel. Integrating this coupling over the internuclear distance gives elements of the interaction matrix $\Psi$:

$$V^{NMA}_{d_j,lN^+v^+}(E) = \langle \chi_{N^+d_j}^A | V^{(e)\Lambda}_{d_j,l} | \chi_{N^+,v^+}^A \rangle,$$

where $E$ is the total energy and $\chi_{d_j}^A$ and $\chi_{N^+,v^+}^A$ are the nuclear wave-functions corresponding to a dissociative state and to an ionization channel, respectively. This procedure applies in each $\Lambda$-subspace, and results in a block-diagonal global interaction matrix. Starting from the
interaction matrix $\mathbf{V}$ and from the zero-order Hamiltonian $H_0$, we build the reaction $K$-matrix, which satisfies the Lippmann-Schwinger equation [32]:

$$K = V + V \frac{1}{E - H_0} K.$$  

In order to express the result of the short-range interaction in terms of phase-shifts, we perform a unitary transformation of our initial basis into a new one, corresponding to eigenchannels, via the diagonalization of the reaction matrix $K$:

$$K \mathbf{U} = -\frac{1}{\pi} \tan(\eta) \mathbf{U}.$$  

In the external ‘B-region’ [31] the Born-Oppenheimer model is no longer valid for the neutral molecule, and a frame transformation [33, 34, 35, 36] is performed, via the projection coefficients (having neglected the partial wave mixing [36, 37]):

$$C_{\Lambda \Lambda', \Lambda, \Lambda'} = \left( \frac{2N+1}{2N+1} \right)^{1/2} \left( \Lambda - \Lambda' \right) N^+ \Lambda^+ |N^+ N\Lambda \rangle \times \sum_{\Lambda' \Lambda} U_{\Lambda, \Lambda'} \langle \chi_{N^+ \Lambda'} \cos(\pi \mu \lambda) + \eta_{\Lambda} \rangle |\chi_{N\Lambda'} \rangle.$$  

Figure 1. HD$^+$/HD states (potential energy curves and vibrational levels) relevant for the electron/HD$^+$ reactive collisions: HD$^+ 2\Sigma_g^+(1s\sigma_g)$ (blue), HD$^+ 2\Sigma_u^+(2p\sigma_u)$ (orange), HD$^{**} 1\Sigma_g^+(2p\sigma_u^2)$ dissociative state (red), and HD$^* 1\Sigma_g^+(1s\sigma_g, 5s\sigma_g)$ Rydberg state (green). The violet lines represent illustrative values of the total energy of the system, see the text.
\[ C_{d,j;\Lambda \alpha} = U_{d,j;\alpha}^\Lambda \cos \eta_{\alpha}^\Lambda, \]  

which can be organized in a matrix \( C \). The other projection coefficients organized in a matrix \( S \), are obtained as \( S_{\Lambda N^+ + v^+;\Lambda \alpha} \) and \( S_{d,j;\alpha} \) by replacing cosine with sine in Eqs. (7) and (8). In these equations, the quantities \( \tau^+ \) and \( \tau \) are related to the reflection symmetry of the ion and neutral wave function respectively, and take the values +1/ −1 for symmetric/antisymmetric states respectively.

Matrices \( C \) and \( S \) are the building blocks of the generalized scattering matrix \( X \), involving all the channels, open (‘o’) and closed (‘c’), and organized in 4 sub-matrices:

\[ X = \begin{pmatrix} C + iS \\ C - iS \end{pmatrix}, \quad X = \begin{pmatrix} X_{oo} & X_{oc} \\ X_{co} & X_{cc} \end{pmatrix}. \]

(9)

Imposing boundary conditions leads to the physical scattering matrix [26]:

\[ S = X_{oo} - X_{oc} \frac{1}{X_{cc} - \exp(-i2\pi\nu)} X_{co}, \]

(10)

where the diagonal matrix \( \exp(-i2\pi\nu) \) is formed with the effective quantum numbers \( \nu_{N^+ + v^+} = [2(E_{N^+ + v^+} - E)]^{-1/2} \) (in atomic units) associated with each vibrational threshold \( E_{N^+ + v^+} \) of the ion situated above the current energy \( E \) (and consequently labeling a closed channel).

For a molecular ion initially in the level \( N_i^+ v_i^+ \) and recombining with an electron of kinetic (collision) energy \( \varepsilon \), the cross section of capture into all the dissociative states \( d_j \) of the same symmetry is given by

\[ \sigma_{N^+ v^+_i \rightarrow N^+ v^+_i}^{N, \text{sym}} = \frac{\pi}{4\varepsilon} \frac{2N + 1}{2N_i^+ + 1} \rho_{\text{sym}}^\Lambda \sum_{l,j} |S_{d,j;l}^{\Lambda N^+ v^+_i}|^2. \]  

(11)

On the other hand, the cross section for a ro-vibrational transition to the final level \( N_f^+ v_f^+ \), giving elastic scattering or (de-)excitation, writes:

\[ \sigma_{N^+_f v^+_f \rightarrow N^+_i v^+_i}^{N, \text{sym}} = \frac{\pi}{4\varepsilon} \frac{2N + 1}{2N_i^+ + 1} \rho_{\text{sym}}^\Lambda \times \sum_{l',l',\Lambda,j} |S_{N_i^+ v_i^+;N_f^+ v_f^+}^{\Lambda X} - \delta_{N_i^+ N_f^+} \delta_{v_i^+ v_f^+} \delta_{l'l'}|^2. \]

(12)

Here \( \rho_{\text{sym}} \) is the ratio between the multiplicities of the neutral and the target ion. After performing the MQDT calculation for all accessible total rotational quantum numbers \( N \) and for all the relevant symmetries, one has to add up the corresponding cross sections in order to obtain the global cross section for dissociative recombination or ro-vibrational (de-)excitation as a function of the electron collision energy \( \varepsilon \).

When rotational excitation and rotational couplings are neglected - the so-called ”non-rotational case” - the formalism becomes much simpler. Moreover, one has to perform separate calculation within each symmetry block \( \Lambda \) and eventually sum over this quantum number the resulting cross sections. For a given \( \Lambda \), the previous formulae become:

\[ \wp_{d_j;l;\nu;\Lambda}(E) = \langle \chi_{d_j}^{\Lambda} | \psi_{\nu;\Lambda}(E) \rangle, \]

\[ C_{\nu;\Lambda} = \sum_{v} U_{\nu;v;\Lambda}(\chi_{\nu;+}(R)| \cos(\pi \mu_i^\Lambda(R) + \eta_\alpha^\Lambda)|\chi_{\nu}(R)), \quad C_{d;\Lambda \alpha} = U_{d;\alpha}^{\Lambda} \cos \eta_\alpha^\Lambda, \]

(13)

(14)
Dissociative recombination of $^2\Sigma^+_g (1s\sigma_g) v_j^+=0$ HD$^+$ ion. Blue (upper)/red (lower) curves: dissociative excitation neglected/accounted, dashed/solid corresponding to first-order/second-order calculations respectively. Black dot-dashed curve: computation of Takagi [36]. Circles: Experiment by Tanabe et al [37]. Triangles: Experiment by Al-Khalili et al [38] (See Ref [39] for more details).

\[
\sigma^\text{sym, } \Lambda_{\text{diss} \rightarrow v_i^+} = \frac{\pi}{4\varepsilon} \rho^\text{sym, } \Lambda \sum_{l,j} |S^\Lambda_{d_j, l_j v_i^+}|^2, \quad \sigma^\text{sym, } \Lambda_{\text{diss} \rightarrow v_i^+} = \sum_{\Lambda} \sigma^\text{sym, } \Lambda_{\text{diss} \rightarrow v_i^+},
\]

The cross section for vibrational transition - elastic scattering or vibrational (de-)excitation - is expressed as:

\[
\sigma^\text{sym, } \Lambda_{v_j^+ \rightarrow v_i} = \frac{\pi}{4\varepsilon} \rho^\text{sym, } \Lambda \sum_{l,l'} |S^\Lambda_{l v_j^+, l' v_i} - \delta_{l,l'} \delta_{v_j^+, v_i}|^2, \quad \sigma^\text{sym, } \Lambda_{v_j^+ \rightarrow v_i} = \sum_{\Lambda, \text{sym}} \sigma^\text{sym, } \Lambda_{v_j^+ \rightarrow v_i},
\]

At energies higher than the dissociation threshold of the ion - e.g. $E_3$ in Figure 1 - we have to allow for the autoionization with respect to ion states from the continuum part of the vibrational spectrum, i.e. dissociative excitation (DE) [39]. For the relevant electronic states of the ionic core, we discretize their vibrational continua by adding a high potential energy wall at a large internuclear distance. With respect to the formalism outlined above, this increases the number of the ionization channels pertaining to the ground electronic state of the ion - see the quasi-continuum spectrum of vibrational levels in blue in Figure 1, responsible in our model for the "Dissociative Excitation of the first kind", DE1. Moreover, if excited electronic states of the ion are available, they will imply the inclusion of new series of ionization channels - see the quasi-continuum spectrum of vibrational levels in orange in the same figure, supporting the
"Dissociative Excitation of the second kind", DE2. Consequently, significantly more channels and their couplings with respect to the already existing ones at low energy have to be added in the V-, K-, X- and S-matrices displayed in eqs. (4)-(10).

2.2. Electron/HD$^+$ reactive collisions
2.2.1. High energy (above ground-state-ion dissociation threshold)

We have performed extensive calculations of DE-assisted DR cross section for capture into all the dissociative states within all the relevant symmetries, $^1\Sigma^+_g$, $^1\Sigma^+_u$, $^1\Pi_u, g$, and for a broad range of energy, $0 - 12$ eV [39]. The computations have been carried out in the first and second order of the K-matrix, and relied on molecular data previously used [25, 40, 41].

Whereas the capture into Rydberg resonant states AB$^*$ (appearing in the general eq. (1)) is excluded in this energy range, the contribution of the AB$^{*\scriptscriptstyle(c)}$ and AB$^{*\scriptscriptstyle(c)}$ states, related to DE1 and DE2 respectively, is decisive. Their inclusion in the model is performed, as shown in the previous section, by the discretization of the vibrational continua associated to the lowest electronic states of the ionic core, $^2\Sigma^+_g(1s\sigma_g)$ and $^2\Sigma^+_u(2p\sigma_u)$, by adding a 15 eV high potential energy wall at $R = 25$ a$_0$. Our final best result, the full red curve in Fig. 2, is in reasonable agreement with previous theoretical estimations - black dashed-dotted line on the same figure -
2.2.2. Low energy (below ground state ion dissociation threshold)

When the total energy of our molecular system is situated in the discrete part of the vibrational spectrum of the cation, closed channels become available and, consequently, temporary capture into bound AB⁺ states occur. This induces local resonances in the shape of the cross section. For example, for HD, one may notice that the levels \( v = 3 \) and \( v = 12 \) of the Rydberg state having as potential the green curve appearing in Figure 1 are situated at the energies \( E_1 \) and \( E_2 \) respectively, and such resonant features are likely to appear at these total energies.

However, in order to produce accurate low-energy DR rate coefficients, the energy diagram shown in Figure 1 is not sufficiently detailed, since it completely neglects the rotational structure of both HD and HD⁺.

Figures 3 and 4 display our results at incident electron energies close to zero, after taking into account the rotational structure and the corresponding interactions, for the case of the cation in its ground vibrational state, but on the lowest 12 rotational states. One may notice the very rich resonant structures, which we have discussed in detail in Ref. [42]. In experiments [42] at the TSR heavy ion storage ring at the Max Planck Institute für Kernphysik in Heidelberg, the DR rate of HD⁺ ions was measured using merged electron and ion beams as a function of the electron collision energy and compared to the rotationally averaged theoretical results. In the range 0.05 – 0.2 eV, theory was found to reproduce the magnitude and resonant structure of the cross section very well (typical collision energy spread 0.005 – 0.01 eV). Above 0.05 eV collision
energy, some experimental peaks were similarly well reproduced as at higher energies, with some deviations in the structure remaining. Yet, the overall magnitude of the DR rate was reproduced very well also in this energy region. The corresponding Maxwell rate-coefficients are given in Figure 5. A large scatter of the rates at low electron temperature occurs between the rotational level, which becomes smaller for higher electron temperatures. Experimental studies of this rotational dependence of the low-energy electron rate coefficient by state specific measurements in a cryogenic ion storage ring [43] are planned in future work.

2.3. Electron/BeH\(^+\) reactive collisions

After producing the molecular data - potential energy curves and autoionization widths - relevant for the study of the collisions of electrons with diatomic Beryllium Hydride cation, two of the present authors (A. L. and A. E. O.) have performed a time-dependent wave-packet study of the DR [44]. Later, we used this data as input for a series of MQDT calculations of DR, vibrational IC and vibrational SEC cross sections, taking into account the direct and indirect processes [45]. We have considered the target molecular ion in its lowest four vibrational levels \((v_i^+ = 0 - 3)\) of its ground electronic state. The cross sections are calculated separately for each symmetry (involving all the relevant dissociative states within the symmetry) and are summed up to give the global cross section.

We have explored the energy range \(10^{-3} - 2.7\) eV of the incident electron, which corresponds to a total energy of the system below the dissociation limit of its ground electronic state. The rotational structure and interactions have been neglected, which is completely justified by the weak role of the indirect process [35] for this ion. Whereas extensive information is given in Ref.
Figure 6. Dissociative recombination of $^{2}\Sigma_{g}^{+}(1s\sigma_{g}) v_{i}^{+}=0$ HD$^{+}$ ion. Black curve: data displayed on Fig. 3 for $N_{i}^{+} = 0$. Red curve: Averaged calculated cross section of the black curve over $\Delta \epsilon = 0.02$ eV between $\epsilon_{\text{min}} = 0$ eV and $\epsilon_{\text{max}} = 0.35$ eV. Blue curve: Interpolation of averaged cross section by eq. (A.2) (see Tables A1, A2, and A3).

[45] on the cross sections, we focus here on the Maxwell rate coefficients up to 5000 K.

Figure 7 shows the global DR, IC and SEC rate coefficients for the three lowest excited vibrational levels of the ion, in comparison with that corresponding to the ground vibrational state. The rate coefficient for the Vibrational Transitions (VT) - IC and SEC - result from a sum on all the possible final vibrational levels accessible by the reactive scattering. This figure illustrates a relatively fast DR of BeH$^{+}$ in its $v_{i}^{+} = 2$ level, as well as a relatively fast vibrational de-excitation for $v_{i}^{+} = 3$, at low temperature.

Figure 8 gives relevant information on the complete set of state-to-state rate coefficients available for the detailed kinetics of BeH$^{+}$ on its lowest four vibrational states.

2.4. Interpolation and averaging
In order to allow a simple use of the complicated cross sections and rate coefficients, we have averaged them using standard plasma kinetics procedures. They are presented for both electron/HD$^{+}$ and electron/BeH$^{+}$ systems in the Appendix.

3. Photoionization of H$_{2}$
In the present section we report theoretical photoionization cross sections for excitation from excited vibrational levels of the ground state. Our calculations are based on MQDT [29] which
Figure 7. Vibrational dependence of the global DR, VE and VdE rate coefficients of BeH+ ($v^+_i$ stands for the vibrational quantum number of the target ion).

allows us to take account of the full manifold of Rydberg states and their interactions with the electronic continuum. We show that the photoionization cross section is actually dominated by resonance effects, in the sense that autoionizing resonances produce a major fraction of the averaged cross section. The same kind of patterns are present in the dissociative recombination of the molecular cations with low energy electrons, whenever the DR is determined by resonant capture into Rydberg states.

The present report deals with the Q transitions ($\Delta N = 0$) which account for roughly one third of the total photoabsorption cross section. We focus in particular on the role of the resonances in the photoionization cross sections, and we choose $v'' = 1, N'' = 1$ to exemplify this. Analogous results dealing with the Q, P and R optical dipole transitions will be published soon, including an extensive ensemble of transition energies, Einstein A coefficients as well as photoionization cross sections and Rydberg resonance parameters for various $v''$, $N''$ values.

3.1. The global MQDT-type approach

In this section, we closely follow the derivations given in Ref [9]. The manifold of $^1\Pi_u$ excited states of H$_2$ is assumed to represent a single unperturbed $n\pi\sigma$ Rydberg series converging to the $X^2\Sigma_g^+$ ground state of H$_2^+$. The quantum defects may thus be extracted directly from the clamped-nuclei (Born-Oppenheimer) potential energy curves (PEC) by use of the one-channel Rydberg equation, written here in atomic units as a geometry-dependent function:

$$U_n(R) = U^+(R) - \frac{1}{2[n - \mu_n(R)]^2}. \quad (18)$$

The index $n$ of the quantum defect $\mu$ indicates that this quantity may vary slightly with the principal quantum number $n$, i.e., it is energy-dependent. This energy dependence is formally
Figure 8. Dissociative recombination and state-to-state vibrational (de-)excitation rate coefficients of BeH$^+$ initially in one of its four lowest vibrational levels, $v_i^+$. For each initial vibrational state of BeH$^+$, the final vibrational quantum numbers are indicated for de-excitation and for the first three (from the left to the right) vibrational excitation curves. For the remaining unlabeled curves, their order corresponds to the successive increase of the vibrational quantum numbers of the target cation.

parametrized as an expansion in terms of the electron binding energy $\epsilon$ (in a.u.):

$$
\mu(\epsilon, R) = \mu(0)(R) + \epsilon \mu(1)(R) + \frac{\epsilon^2}{2} \mu(2)(R) + \frac{m}{M} \mu^{\text{spec}}(R).
$$

(19)

The three coefficients $\mu^{(k)}(R), k = 0, 1, 2$ that appear in Eq. (19) are determined by means of Eq. (18) from the three clamped nuclei PEC, $U_n(R)$, of the $n\pi, n = 2, 3, 4$ Rydberg states computed by Wolniewicz and co-workers [46, 47, 48], combined with the PEC, $U^+(R)$, of the ion ground state $X^2\Sigma_{g}^+$. The clamped-nuclei electron binding energy is given for each $R$-value by the difference $\epsilon = \epsilon(R) = U_n(R) - U^+(R)$. $\mu^{\text{spec}}(R)$ is related to the mass polarization term arising from the cross-term $H_3' = -(m/4M) \nabla_1 \nabla_2$ of the molecular Hamiltonian [49] ($m$ electron mass, $M$ nuclear reduced mass). $H_3'(R)$ has also been evaluated ab initio by Wolniewicz and co-workers [48].

The electronic dipole transition moments constitute a second set of input data required for the description of radiative electronic transitions. Energy dependent clamped-nuclei electronic channel transition moments are parametrized in analogy with Eq. (19) as

$$
d(\epsilon, R) = d(0)(R) + \epsilon d(1)(R) + \frac{\epsilon^2}{2} d(2)(R).
$$

(20)

These quantities are energy normalized and have the dimension $[\text{length}] \times [\text{energy}]^{-1/2}$. The coefficients $d^{(q)}(R), q = 0, 1, 2$, may be derived directly from the ab initio clamped-nuclei dipole transition moments of Wolniewicz and co-workers [47, 48], see Refs. [9, 50].
Upper state energy levels and/or continuum states and the rovibronic dipole transitions leading to them are computed using standard MQDT techniques [9, 27, 28, 29]. The transition of the excited electron from the molecule-fixed reference frame to the space-fixed frame is described by a frame transformation which takes account of the non-adiabatic effects. In the case of the $Q(N)$ spectral lines corresponding to upper states of pure $^1\Pi_u^-$ symmetry there is no rotational non-adiabatic coupling so that, neglecting spin-orbit and hyperfine effects, the frame transformation reduces to evaluating integrals involving the initial and final state vibrational wave functions:

$$
\mu^{(q,N,d)}_{v^+N+,v'^+N'^+} = \int \chi_{v^+N+}^{(q)}(R)\mu^{(q)}(R)\chi_{v'^+N'^+}(R)dR,
$$

for the vibronic quantum defect, and:

$$
d^{(q,N,d)}_{v^+N+,v'^+N'^+} = \int \chi_{v^+N+}^{(q)}(R)d^{(q)}(R)\chi_{v'^+N'^+}(R)dR,
$$

for the vibronic transition moments. Here $q = 0, 1, 2$ as in Eqs. (19) and (20). The $Q(N)$ transitions studied here require that the total angular momenta of the molecule $N', N''$ and of the molecular ion $N^+, N'^+$ all be equal, i.e., $N = N^+ = N'^+ = N''$. $d$ refers to the Kronig’s symmetry label, designating levels that have total parity $(-1)^N$.

The energy dependences of the vibronic quantum defects and dipole moment matrix elements of Eqs. (21) and (22) have the same functional form as those given in the Eqs. (19) and (20), with the difference that instead of $\epsilon$ one must use a vibrationally averaged value, $\overline{\epsilon}$. For the quantum defects the appropriate choice is $\overline{\epsilon} = \frac{1}{2} \left( E - E^+_{v^+N^+} \right) + \left( E - E^+_{v'^+N'^+} \right)$ [29], where $E$ denotes the total energy and $E^+_{v^+N^+}$ are the vibration-rotation levels of the ion ground state. For the transition moments one chooses $\overline{\epsilon} = \left( E - E^+_{v^+N^+} \right)$ [29]. Once the rovibronic quantum defect have been evaluated they must be converted into the so called $S$ and $C$ matrices which are related to the reaction matrix $K$ according to $K = SC^{-1}$. This is achieved by means of procedures described in Refs. [51] and [52]. The “eigenchannel” formulation of MQDT [29] rewrites these matrices in the form $S = U \sin \pi \mu UT$ and $C = U \cos \pi \mu UT$, where $U$ is the eigenvector matrix of the reaction matrix $K$ while $\tan \pi \mu_{\alpha}$ are its eigenvalues and their arguments $\mu_{\alpha}$ are the associated eigenquantum defects. (The indices $\alpha$ indicate that these quantities are not to be confused with the quantum defects that appear in Eqs. (19) and (21)).

Applying the asymptotic boundary conditions to the total wave function, one arrives at the generalized eigenvalue system [29]:

$$
\Gamma \beta B = \tan \beta \Lambda B,
$$

where

$$
\begin{align*}
\Gamma_{ii'} &= \sin \beta_i C_{ii'} + \cos \beta_i S_{ii'} & i \in \text{closed} \\
\Lambda_{ii'} &= 0 & i \in \text{closed} \\
\Gamma_{ii'} &= S_{ii'} & i \in \text{open} \\
\Lambda_{ii'} &= C_{ii'} & i \in \text{open} \\
\beta_i &= -\pi \nu_i & i \in \text{closed} \\
\beta_i &= +\pi \tau_i & i \in \text{open}
\end{align*}
$$

(24)

If bound levels and discrete line intensities are to be evaluated (because there are no open channels or because open channels are neglected), Eq. (24) reduces to a homogenous set of linear equations, namely

$$
\sum_k \left[ \cos(\pi \nu_j) S_{jk} + \sin(\pi \nu_j) C_{jk} \right] B_k(E) = 0,
$$

(25)
where \( \nu_j(E) = \sqrt{-\mathcal{R} \hbar c/(E - E_j^+)} \) are the channel effective quantum numbers, \( B_k \) are the channel mixing coefficients and \( \mathcal{R} \) is the Rydberg constant. The indices \( j \) and \( k \) run over all vibrational channels \( v^+N^+ \) corresponding to the given \( N^+ \) value. By searching for zeros of Eq. (25) one finds the energies \( E_n \) of the bound levels and the corresponding channel mixing coefficients. The former, in wave number units and defined relative to the ionization thresholds, are

\[
\left[ \left( E_n - E_{v+}^{+N+} \right)/\hbar c \right] = \frac{\mathcal{R}_H}{[\nu_{v+}^{N+}(E)]^2}. \tag{26}
\]

\( \mathcal{R}_H \) here is the mass-corrected Rydberg constant. The effective transition moment to the bound Rydberg state \( n \) is given by the following superposition of channel amplitudes:

\[
D_n = \frac{1}{N} \sum_k d_{kk'}(E_n)B_k(E_n), \tag{27}
\]

where \( k \) stands for the ionization channels \( (v^+N^+) \) and \( k' \) stands for the lower state \( (v'^Nn) \), respectively. \( d_{kk'}(E_n) \) is the frame transformed vibronic dipole moment. \( N \) is the overall normalization factor of the bound-state wave functions, see Ref. [29]. It has the dimension \( [\text{energy}]^{-1/2} \) which compensates the dependence \( [\text{energy}]^{-1/2} \) contained in the channel moments \( d_{kk'} \). The transition moment \( D_n \) for each spectral line is finally converted into an upper state emission probability according to [29]:

\[
A_{n\rightarrow v'^Nn'} = \frac{4mc^2\alpha^5}{\hbar} \left( \frac{1}{2N'+1} \right) \left( \frac{E_n - E_{v'^Nn'}}{2\mathcal{R}\hbar c} \right)^3 \frac{|D_n|^2}{a_0}, \tag{28}
\]

where \( \alpha \) here denotes the fine structure constant.

In order to calculate photoabsorption/photoionization cross section, \( \sigma_a/\sigma_i \), we have to consider the open ionization channels in addition to their closed counterparts. The quantization condition for an open channel \( j \), see Eqs. (23) and (24), reads [29]

\[
\sum_k \left[ \cos(\pi\tau_p)S_{jk} - \sin(\pi\tau_p)C_{jk} \right] B_k^{(\rho)}(E) = 0, \tag{29}
\]

where \( \tau_p \) is an open-channel ionization eigenphase and \( \rho \) is a solution index. In all, there are as many eigenphases as there are open channels, \( N_p \), and there is a set of channel mixing coefficients, \( B_k^{(\rho)} \), corresponding to each particular eigenphase. The total photoionization intensity is expressed in terms of a set of real dipole amplitudes which replace Eq. (27):

\[
D^{(\rho)}(E) = \sum_k d_{kk'}^{(\rho)}(E)B_k^{(\rho)}(E). \tag{30}
\]

The apparent disagreement between Eqs. (27) and (30) reflects the different normalization of the discrete and continuum wave functions: \( D^{(\rho)}(E) \) in Eq. (30) gives the dipole amplitude per unit energy and has dimension \( [\text{length}] \times [\text{energy}]^{-1/2} \). The total photoabsorption cross section, \( \sigma_a \) (equal to the photoionization cross section \( \sigma_i \) when no competing decay channels are present), becomes [29]

\[
\sigma_a(E) = \frac{4\pi^2\alpha}{2N'+1} \left( E - E_{v+}^{+N+} \right) [D(E)]^2, \tag{31}
\]

where \( [D(E)]^2 = \sum_{\rho=1}^{N_p} [D^{(\rho)}(E)]^2 \).
Figure 9. Cross sections and line intensities for the Q(1) transitions from the \( X^1\Sigma_g^+, v'' = 1 \) ground state of the \( \text{H}_2 \) molecule, compiled from [9]. The vertical dotted lines represent the vibrational ionization thresholds, starting with \( v^+ = 0 \) and ending with \( v^+ = 14 \). The vertical continuous line (blue online) indicates the position of the \( \text{H}(1) + \text{H}(n = 3) \) dissociation limit of \( \text{H}_2 \). a) Continuum photoionization cross section. b) Spontaneous emission coefficients for the transitions listed in Ref. [9], equivalent to the resonant part of the cross section. c) Photoionization: continuous black lines: background cross section; dashed line (red online): averaged full cross section.

3.2. Results on \( \text{H}_2 \) photoionization

A more elaborated presentation of the theory can be found in [29, 9], while the methodology of the calculations is presented in [9]. In what follows we will focus on the presentation of theoretical photoionization cross sections for Q transitions (\( \Delta N = 0 \)) from the ground electronic state (\( v'' = 1, N'' = 1 \)). The results obtained rely on the use of the MQDT package developed by Ch. Junge.

By the inclusion of the open channels in addition to the closed ones, and solving Eq. (23) in its most general form, the continuum phase shifts, channel mixing coefficients, effective transition moments are provided and, as the final result, the photoionization cross sections as a function of the transition energy are calculated. Strictly speaking, the theoretical photoabsorption spectrum is produced, which is broadened by interaction with the open ionization continua, in other words photoabsorption eventually results in ionization whenever the two additional decay channels (dissociation and fluorescence) are neglected. Fig. 9a displays the corresponding continuous distribution. In order to calculate the true photoionization cross section, the continuous spectrum has been corrected for dissociation and fluorescence processes. This was performed by using the data from Refs. [7, 8], where absolute cross sections for the competing decay-channels...
fluorescence, dissociation, and ionization of photoexcited long-lived superexcited $\text{H}_2$ molecular levels have been reported from the ionization threshold up to the $n = 3$ dissociation limit. Essentially, we have renormalized the continuous spectrum by multiplying each resonance profile with its corresponding photoionization yield taken from Ref. [8], and thus obtain the photoionization cross section $\sigma_i$.

The plot in Fig. 9a shows that the cross section is dominated by the presence of resonance structures corresponding to excitation of various vibrational levels of bound electronic states which lie above the ionization threshold. A logarithmic intensity scale has been used in order to highlight the density of autoionization structures that arise in the cross section. By representing every discrete upper level by a sharp line with the intensity corresponding to its spontaneous emission probability one obtains the spectrum as a sequence of Feshbach resonances. This can be seen in Figure 9b, where only the lines corresponding to states up to $n = 6$ are given, whereas the total photoionization cross section shown in Fig. 9a contains the states with higher ($n \sim 70$) quantum numbers as well. The overall contribution of the Rydberg resonances of the lowest lying four excited electronic states to the photoionization cross section are summarized in Table II of [9]. It turns out that more than 42% of the total photoionization cross section are produced by the four lowest electronic states.

Fig. 9c is designed to demonstrate the remarkable importance of resonances in the Q(1)
photoionization cross sections. In order to assess the importance of the resonances, we have - for each vibrational interval - calculated the averaged photoionization cross section:

\[ \sigma_i(v^+) = \frac{\int_{E_{v^+}}^{E_{v^+1}} \sigma_i(E) dE}{E_{v^+1} - E_{v^+}}, \]  

indicated in the figure by dashed (red online) line. The black solid line represents the background cross section (direct ionization), obtained when all closed channels are excluded in the calculation and hence all resonances disappear from the spectrum.

We found that at certain photon energies, just above the \( n = 3 \) dissociation threshold (blue continuous vertical line), the resonance enhancement exceeds the background cross section by more than one order of magnitude, while at lower energy (for instance, in the range between the \( v^+ = 1 \) and \( v^+ = 2 \) thresholds) as well as at higher energies this is still more than a factor of two larger than the latter. The total enhancement on the whole energy range exceeds with more then a factor of 6 the background cross section.

The surprising feature that the most intense lines of the spectrum lying at low energies contribute less to the photoionization cross section can be understood from the fact that, as
displayed in Figure 8 of [8] for the lowest lying excited states, the fluorescence dominates for $n = 3$ (D state) and is also present in the $n = 4$ and 5 (D' and D'' states). Photodissociation is significant ($\approx 15$ to $20\%$) for $n = 3$, but is absent for $n = 4$ and 5. Photoionization is dominant for $n \geq 5$. Thus, for instance, in the energy range between the $v^+ = 1$ and $v^+ = 2$ thresholds, the most intense lines, corresponding to the $3p\pi D$ state, result from a strong decay by fluorescence and consequently, do not contribute to the photoionization.

An other key issue in these photo-induced reactions is to produce results which are resolved with respect to the vibrational level ($v^\pm$) of the resulting H$_2^\pm$ ion. These partial cross sections are in particularly important in the kinetic models of the primordial universe chemistry [16].

Figures 10 and 11 display the final state vibrationally resolved photoionization cross sections for the lowest five vibrational levels of the ground state of the molecular ion. The black curve labels the total photoionization cross section, while the colored ones those with $v^+ = 0 - 4$ from the top to the bottom. Due to favorable Frank-Condor overlaps, the partial cross sections are not restricted to a single energy interval (belonging to the same ionization threshold), but can be spread out in the higher energy regions as well (belonging to higher ionization thresholds).

4. Electron/H$_2$ reactive collisions

4.1. The experimental method

We present experimental results on electron-impact dissociation of H$_2$ molecules. We have used a molecular nozzle beam in order to produce molecules with cold internal degrees of freedom with high intensity flux conditions.

The basic layout of the experimental setup, whose detailed description is given in [11] is equivalent to the classical one [54] for time-of-flight (TOF) studies of H(2$^2S_{1/2}$) produced by electron impact on H$_2$, i.e. a hydrogen jet crossing an electron beam at right angle. The H$_2$ beam is produced by a Campargue-type supersonic jet source [55], allowing to get a reduced velocity spread and a well defined initial molecular state and target density. In the chamber where the interaction with the electrons takes place, the pressure is maintained at $5 \times 10^{-7}$ torr , when the supersonic beam is not in operation, and $1.2 \times 10^{-6}$ torr, when the supersonic beam is in operation, by a 2000 l/s diffusion pump. The measured average velocity of the hydrogen molecules in the supersonic jet is 2.7 km/s with $\Delta v/v \sim 1\%$. The beam has a rotational temperature of about 1 K and a vibrational temperature of about 10 K. Due to the expansion, essentially all hydrogen molecules are in the $v = 0$ vibrational level, with relative rotational populations that depend drastically on the detail of the expansion dynamics but are mainly restricted to the states $J = 0$, parahydrogen and $J = 1$, orthohydrogen [56, 57, 58]. In the region where the molecular beam crosses the electron beam, its diameter is approximately 3 mm, and the flow is estimated to be about $10^{22}$ molecules per steradian per second, which corresponds to $(2.3 \pm 0.2) \times 10^3$ molecules per microsecond per cubic millimeter in the interaction volume. The pulsed electron gun consists of a 150 $\mu$m diameter thoriated-tungsten filament, a grid and a collimator with a circular aperture of 2 mm radius, and produces an electron beam with an angular spread FWHM of 5°. The electron beam is detected by a Faraday cup at a distance of 70 mm and produces a typical average current of 2 mA in continuous operation, for 120 V acceleration. The electron beam can be pulsed by applying a negative step voltage, whose duration can be chosen in the range 0.2 to 2 $\mu$sec, to the filament’s DC circuit, which is otherwise maintained positive in order to reduce the electron background. The typical pulse rate is 10 kHz. The electron energy is given by the difference between the potential of the filament and that of the interaction region, which has to be grounded in order to avoid the disappearance of H(2$^2S_{1/2}$) atoms through the very efficient coupling with radiative H(2$^2P_{1/2}$) states. The energy spread of the electron beam is estimated to be of about 6 eV, taking into account the voltage drop in the directly heated filament. This low resolution has no significant effect at high electron energies, as we do not intend to perform precise cross section measurements near threshold. One may also notice that...
the coherent energy width corresponding to $\Delta E = \frac{\hbar}{\Delta t}$ is of the order of 10 eV for electron energies of 100 eV, assuming a size of the hydrogen molecules of few atomic units.

The detection of the metastable $\text{H}(2^2S_{1/2})$ atoms is performed by a specially devised detection system optimized in order to get a well defined detection zone whose distance was chosen to be 230 mm and 254 mm away from the collision zone. We have cross checked the TOF measurements with two detectors working at the same time, which reduces the uncertainties concerning the exact determination of the flight distances. Within this distance range excited $\text{H}(2^2P_{1/2})$ atoms do not reach the detection zone, as their lifetime is 1.7 ns, to be compared with typical TOF of few $\mu$sec for the fastest atoms. As these experiments were designed in order to search for coincidence events between pairs of twin atoms, care is taken to place the detectors in positions consistent with the expected recoil of the superexcited $\text{H}_2$ molecules after collision with the electrons, before dissociation.

A collimator of 2 mm diameter is placed at the entrance of each detection system, and is followed by a pair of needles normal to the direction of $\text{H}(2^2S_{1/2})$ atoms. The potential difference applied to these needles was chosen to be 200 V and produces an electrostatic field of maximum value $4 \times 10^4$ V/m that mixes the $2^2S_{1/2}$ and the $2^2P_{1/2}$ states of the atoms, inducing the decay to the $1^2S_{1/2}$ state and consequently producing Lyman-$\alpha$ radiation (1216 Å). In order to lower the direct photon counts originating from the de-excitation of short lived atomic states and of the radiative molecular states, a channel electron multiplier detector of 10 mm aperture is oriented at right angles with respect to the atom trajectories and to the needles. It is located 4 mm away from the needles. The emitted Lyman-$\alpha$ radiation passes through a grid and a MgF$_2$ plate that shields the channeltron against massive species such as electrons and ions. The efficiency of the detection system is of the order of 0.3%, including intrinsic detector efficiency, effective solid angle seen by the Lyman-$\alpha$ radiation, plate transparency and grid transmission. The quenching

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure12.png}
\caption{Typical Time of flight spectrum [11] for 126 eV electron energy.}
\end{figure}
electric field profile inside the detection system acts in a very localized region of the order of 10 µm and located about 10 µm in front of the needle axis for atoms with velocities in the range of a few dozens of km/s and needle voltages in the 10 – 500 V range. The uncertainty on the total flight length is given by the size of the interaction zone between the electron and the molecular beams, i.e. 2 mm, and consequently the main uncertainty in the time of flight is due to the electron pulse duration: our best resolved peak involves an electron pulse of 0.25 µs duration with a flight length distance of 254 mm, which leads to a peak with a maximum around 8.0 µs and consequently to a TOF uncertainty of 0.125 µs/8.0 µs ≈ 1.7%.

Pulses from the detectors are separately pre-amplified and amplified by standard NIM electronics. After discrimination from electronic noise, the signals are fed as stop pulses of a “FAST ComTec” multichannel analyzer card. The detector pulses are also analyzed in parallel, after pre-amplification, by a fast oscilloscope. Particular care was taken that the average pulse heights had a uniform non saturated value over all the observation range. Indeed, saturation effects such as bleaching can arise because of the huge peak associated with the electron pulse.

**Figure 13.** Time-of-flight spectra [11] of H(2^2S) atoms dissociated from H₂.
Figure 14. (a) Energy spectra for the fast atoms with the same counting time intervals, for different electron collision energy. From bottom to top: 26, 36, 46, 66, 86, 106 and 126 eV. (b) We display (vertical axis in arbitrary units) $I \times E_e$, where $I = \int_{\text{Fast peak}} N(E) dE / V_{\text{Faraday cup}}$, which is proportional to the H(2S) production, from [11].

4.2. Results on electron-impact / $H_2$ dissociation

The experimental time-of-flight spectrum obtained for electron collision energy of 126 eV that we have used for calibration of our data is presented in Fig.12 for the detector at 254 mm from the collision center. In this spectrum, one can distinguish three main regions corresponding to increasing time-of-flights: (i) a very bright peak related to the electron gun pulse, in width and intensity, (ii) a contribution of fast atoms, and (iii) a contribution of slow atoms at a larger time-of-flight, which is quite as well resolved as the spectra obtained by photoabsorption [59] and whose structures are analyzed in [63].

Experimental TOF spectra obtained for electron collision energies between 10 and 126 eV are presented in Fig. 13. They correspond to the measurements of one detector, normalized both to electron beam current and acquisition time, for the detector at 230 mm from the collision center.

In these spectra the traditional classification of the metastable H(2S) atoms into “slow” (velocities of about 10 km/s) and “fast” (velocities of about 35 km/s) is evident, as well as their energetic thresholds: while the slow atoms arising from the singly excited states are visible in our entire energy range, the fast atoms, originating from the doubly excited states, require electron energies greater than 30 eV.

In order to express the data of Fig. 13 as a function of $E_H$, the kinetic energy of the H(2S) atoms in the center-of-mass reference frame, we need to describe the kinematics of the
Table 1. Maximum location of the fast atoms peak [11].

| Date  | Authors                        | Maximum position (eV) | Peak width (eV) | Electron energy (eV) |
|-------|--------------------------------|-----------------------|-----------------|----------------------|
| 1967  | Leventhal, Robiscoe & Lea [54] | 4.7±0.7               | 2.6             | 60                   |
| 1972  | Misakian & Zorn [60]           | 4.5±0.5               | 2.8             | 70                   |
| 1977  | Carnahan & Zipf [61]           | 5.1±0.4               | 3.1             | 75                   |
| 1977  | Carnahan & Zipf [61]           | 5.3±0.4               | 3.4             | 100                  |
| 1977  | Hazi & Wiemers [62]            | 4.8±0.4               | 2.6             | 100                  |
| 1980  | Spezeski, Kalman & McIntyre Jr. [53] | 5.6±0.4           | 3.7             | 98                   |
| 2011  | Medina et al [11]              | 5.6±0.2               | 3.3             | 126                  |
| 2011  | Medina et al [11]              | 5.5±0.5               | 3.2             | 106                  |
| 2011  | Medina et al [11]              | 5.4±0.5               | 3.3             | 86                   |
| 2011  | Medina et al [11]              | 5.4±0.5               | 3.4             | 66                   |
| 2011  | Medina et al [11]              | 5.0±0.5               | 3.8             | 46                   |
| 2011  | Medina et al [11]              | 4.9±0.5               | 3.1             | 36                   |

Experimental conditions:
- ref. [54]: $\theta = 77^\circ$ and $90^\circ$, $\tau_e = 0.2$ $\mu$s and $L = 10$ cm.
- ref. [60]: $\theta = 80^\circ$, $\tau_e = 0.5$ $\mu$s and $L = 13.14 \pm 0.24$ cm.
- ref. [61]: $\theta = 90^\circ$, $\tau_e = 0.4$ $\mu$s and $L = 28$ cm.
- ref. [53]: $\theta = 90^\circ$, $\tau_e = 0.1$ $\mu$s and $L = 18.3 \pm 0.3$ cm.
- ref. [11]: for $E_e = 126$ eV; $\theta = 90^\circ$, $\tau_e = 0.25$ $\mu$s and $L = 25.4 \pm 0.1$ cm.
- ref. [11]: for $E_e = 106 – 36$ eV; $\theta = 90^\circ$, $\tau_e = 0.5$ $\mu$s and $L = 23.0 \pm 0.1$ cm,

with $E_e$ the electron energy of the electron beam, $\theta$ the angle between the direction where the metastable atoms are detected and the electron-beam axis, $\tau_e$ the time duration of the electron pulse and $L$ the distance between the collision region and the quenching region or the detector itself (TOF distance). The uncertainties displayed above, in the maximum position (in eV), are a consequence of the uncertainties in these quantities and of the electron pulse width, and their values were extracted from ref. [53]. The pressure used in all works was in the range of $10^{-4} – 10^{-5}$ torr.

In our experiments, the position of the detectors was chosen so that to select hydrogen atoms produced by dissociation with velocities orthogonal to the plane defined by molecular and the electron beams. The inversion of the spectra requires some care for the slow atom part [63] but is easy for the fast atom part that we will focus on.

In these spectra - Fig. 14 - where the components of the peak are not resolved, one can assume a smooth evolution of the location of the maximum of the peak from low to high energies, which saturates at energies higher than 60 eV (about twice the mean threshold energy). The TOF spectra are not sensitive to the temperature of the H$_2$ gas as one can see from previous works on these processes summarized with our contributions in Table 1.

In these results, the production of the fast metastable hydrogen atoms has been studied as a function of the variation of the electron energy with two detectors. Using uncorrelated detectors, we have observed that the signal intensities are angle-independent. This will be no longer the case for future coincidence experiments with correlated detectors, because this configuration corresponds to the selection of definite values for the direction of the interatomic vector in the center-of-mass frame. This angular dependence will reflect the angular momentum conservation rules of the electron-molecule excitation process. For instance it will allow us to determine the dependence of the production of the atom pairs with respect to the forward (small electron-molecule impact parameters) or backward (high electron-molecule impact parameters) processes.
5. Conclusion and perspectives

Using the Multichannel Quantum Defect Theory, we have computed cross sections and rate coefficients for dissociative recombination, vibrational excitation and de-excitation for HD$^+$ and BeH$^+$, and dissociative excitation for HD$^+$. The computed cross sections for HD$^+/\text{HD}$ system are in good agreement with the measurements. We plan to complete the data set for this system, carrying out calculations with a careful state-to-state analysis for a broad range of energies. This represents a significant computational effort which is currently in progress.

By calculating the photoionization cross section from the vibrationally excited ground electronic state of the hydrogen molecule, we have shown that in contrast to what had been assumed previously, autoionization resonances dominate the cross section. Moreover we have determined the final state vibrationally resolved cross sections in order to estimate the level populations of the produced molecular ions.

The raw data corresponding to the figures related to the electron-molecular cation reactive collisions and to the photoionization (Figs. 2−10) are available on demand.

We have revisited previous work on dissociation by electron impact of the H$_2$ molecule leading to one H(2$^2S_{1/2}$) atom. Uncorrelated detectors lead to isotropic spectra. Coincidence experiments will select specific interatomic directions related to an unique molecule for each event. Accurate analysis of the data with detectors selectively sensitive to protons or to metastable or Rydberg atoms will provide refined and quantitative information on the dynamics of these superexcited states versus the Coulomb explosion mechanism [65].

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Appendix

In order to allow a simple use of the complicated physical observables like cross sections or rate coefficients shown for example in Figures 3 and 4, we have averaged them by using the simple formulas

\[
\sigma_{DR,(AB^+),N_i^+}(\epsilon < \epsilon_{max}) = \frac{1}{\Delta \epsilon} \int_{\epsilon - \Delta \epsilon/2}^{\epsilon + \Delta \epsilon/2} \sigma_{DR,(AB^+),N_i^+}(\epsilon') d\epsilon',
\]

between $\epsilon_{min} = 0$ eV and $\epsilon_{max} = 0.35$ eV, where $\Delta \epsilon = 0.02$ eV. This results in smooth cross sections, as for example that shown for the Dissociative Recombination of HD$^+$ in Fig. 6, which can be eventually generated by a polynomial interpolation formula:
\[ \sigma_{DR}^{(AB^+),N_i^+,\Delta \epsilon}(\epsilon < \epsilon_{\text{max}}) = \sigma_{DR}^{(AB^+),N_i^+,\epsilon_{\text{min}} \rightarrow \epsilon_{\text{max}}} \exp \left[ \sum_{j=0}^{45} C_{N_i^+}(j) \left( \epsilon - \epsilon_{\text{min}} \rightarrow \epsilon_{\text{max}} \right)^j \right], \quad (A.2) \]

where the different coefficients for the HD\(^{+}\) ions are tabulated in the Tables A1, A2, and A3. The term \( \sigma_{DR}^{(AB^+),N_i^+,\epsilon_{\text{min}} \rightarrow \epsilon_{\text{max}}} \) is the cross section averaged over the whole energy range \([\epsilon_{\text{min}}, \epsilon_{\text{max}}]\).

And finally, if Maxwell distribution can be assumed, the thermal rate coefficients for the same system displayed in Fig. 5 can be produced by the interpolation formula:

\[ k_{(HD^+),N_i^+}(T_e) = A_{N_i^+} T_e^{\alpha_{N_i^+}} \exp \left[ -\sum_{j=1}^{7} \frac{B_{N_i^+}(j)}{j T_e^j} \right], \quad (A.3) \]

over the electron temperature range \( 10 \text{ K} \leq T_e \leq 5000 \text{ K} \). The parameters \( A_{N_i^+}, \alpha_{N_i^+} \) and \( B_{N_i^+}(j) \) are listed in Table A4.

The calculated rate coefficients of the Dissociative Recombination of BeH\(^{+}\) in each of its first four vibrational states have been interpolated under the mathematical form, similar to eq. (A.3)

\[ k_{(BeH^+),v_i^+}(T_e) = A_{v_i^+} T_e^{\alpha_{v_i^+}} \exp \left[ -\sum_{j=1}^{7} \frac{B_{v_i^+}(j)}{j T_e^j} \right], \quad (A.4) \]

over the electron temperature range \( 100 \text{ K} \leq T_e \leq 5000 \text{ K} \). The parameters \( A_{v_i^+}, \alpha_{v_i^+} \) and \( B_{v_i^+}(j) \) are listed in Table A5.

Using again the (A.3) general formula, the calculated rate coefficients of the Vibrational Excitation of BeH\(^{+}\) have been interpolated under the form

\[ k_{(BeH^+),v_i^+ \rightarrow v_f^+}(T_e) = A_{v_i^+ \rightarrow v_f^+} T_e^{\alpha_{v_i^+ \rightarrow v_f^+}} \exp \left[ -\sum_{j=1}^{7} \frac{B_{v_i^+ \rightarrow v_f^+}(j)}{j T_e^j} \right], \quad (A.5) \]

over the electron temperature range \( 300 \text{ K} \leq T_e \leq 5000 \text{ K} \). The parameters \( A_{v_i^+ \rightarrow v_f^+}, \alpha_{v_i^+ \rightarrow v_f^+} \) and \( B_{v_i^+ \rightarrow v_f^+}(j) \) are listed in Tables A6 and A7.

The values interpolated using the equations (A.3)–(A.5) reproduce the reference values within a few percent, for the listed different rate coefficients.
| \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) | \( N_t^- \) | \( T_{in} \) |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) | \( (H^{-}) \) |
| \( N_t^- \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) | \( (N_e^-) \) |
| \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) | \( C_j \) |
| \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) | \( C_1 \) |
| \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) | \( C_2 \) |
| \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) | \( C_3 \) |
| \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) | \( C_4 \) |
| \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) | \( C_5 \) |

Table A2. Same as Table A1 for \( (N_e^-) \) with \( N_e^- = 5, 6, 7, \) and 8.

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| $N_{\text{N}}^+$ | $T_{\text{in}}$ | $T_{\text{e, out}}$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ | $C_{\text{N}}^+$ |
|----------------|-----------|----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| $9$            | $0.179206617 \times 10^{-14}$ | $0.175000000 \times 10^{-14}$ | $0.24172961 \times 10^{-14}$ | $0.14495109 \times 10^{-12}$ | $0.33115241 \times 10^{-12}$ | $0.49878674 \times 10^{-12}$ | $0.38018063 \times 10^{-12}$ | $0.21860271 \times 10^{-12}$ | $0.82827945 \times 10^{-12}$ | $0.67151789 \times 10^{-12}$ | $0.46891096 \times 10^{-12}$ | $0.12773088 \times 10^{-12}$ |
| $10$           | $0.63075527 \times 10^{-15}$ | $0.175000000 \times 10^{-14}$ | $0.18789245 \times 10^{-14}$ | $0.22104869 \times 10^{-12}$ | $0.58130541 \times 10^{-12}$ | $0.38583764 \times 10^{-12}$ | $0.48258011 \times 10^{-12}$ | $0.24562052 \times 10^{-12}$ | $0.18163313 \times 10^{-12}$ | $0.113090103 \times 10^{-12}$ | $0.56110640 \times 10^{-12}$ | $0.37582277 \times 10^{-12}$ |
| $11$           | $0.26230015 \times 10^{-14}$ | $0.175000000 \times 10^{-14}$ | $0.35414480 \times 10^{-14}$ | $0.50347713 \times 10^{-12}$ | $0.27890904 \times 10^{-12}$ | $0.24760110 \times 10^{-12}$ | $0.32121079 \times 10^{-12}$ | $0.26640390 \times 10^{-12}$ | $0.25096049 \times 10^{-12}$ | $0.113990103 \times 10^{-12}$ | $0.11830917 \times 10^{-12}$ | $0.10701420 \times 10^{-12}$ |
| $12$           | $0.14629004 \times 10^{-14}$ | $0.175000000 \times 10^{-14}$ | $0.31835527 \times 10^{-14}$ | $0.36087012 \times 10^{-12}$ | $0.10934091 \times 10^{-12}$ | $0.87727984 \times 10^{-12}$ | $0.16493051 \times 10^{-12}$ | $0.17790156 \times 10^{-12}$ | $0.14428880 \times 10^{-12}$ | $0.12137905 \times 10^{-12}$ | $0.12378618 \times 10^{-12}$ | $0.16493051 \times 10^{-12}$ |
Table A4. List of the parameters used in Eq. (A3) for the DR rate coefficients of HD⁺, Fig. 5.

| \( \nu \) | \( A_{N_h} \) | \( \sigma_{N_h} \) | \( B_{N_h}^{(1)} \) | \( B_{N_h}^{(2)} \) | \( B_{N_h}^{(3)} \) | \( B_{N_h}^{(4)} \) | \( B_{N_h}^{(5)} \) | \( B_{N_h}^{(6)} \) | \( B_{N_h}^{(7)} \) |
|----------|---------|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 0        | 0.222071374×10⁻⁴ | -0.392864010×10⁻⁴ | 0.73919972×10² | -0.154789113×10⁷ | 0.10315553×10⁷ | -0.316311988×10⁸ | 0.493047262×10⁸ | -0.380243534×10¹⁰ | 0.115087036×10¹¹ |
| 1        | 0.128851757×10⁻⁴ | -0.110758979×10⁻⁴ | 0.171574468×10³ | -0.133254014×10⁸ | 0.63073066×10⁶ | -0.162724863×10⁸ | 0.225708556×10⁸ | -0.161473237×10¹⁰ | 0.465576516×10¹¹ |
| 2        | 0.114310768×10⁻⁴ | -0.109091626×10⁻⁴ | 0.228749416×10⁶ | -0.62620362×10⁶ | 0.26204786×10⁶ | -0.162018×10¹⁰ | -0.29295948×10⁸ | 0.253215411×10¹⁰ | -0.71344532×10¹¹ |
| 3        | 0.210694359×10⁻⁴ | -0.15741172×10⁻⁴ | 0.38733066×10³ | -0.458061947×10⁷ | 0.215862337×10⁸ | -0.524142418×10⁸ | 0.692418139×10⁹ | -0.47234646×10¹⁰ | 0.130101606×10¹¹ |
| 4        | 0.101949901×10⁻⁴ | -0.107653008×10⁻⁴ | 0.259272406×10⁶ | -0.225402550×10⁶ | 0.113744859×10⁷ | -0.330383722×10⁸ | 0.43933765×10⁹ | -0.321416426×10¹⁰ | 0.951009824×10¹¹ |
| 5        | 0.149208014×10⁻⁴ | -0.109088522×10⁻⁴ | 0.14779496×10³ | -0.107365043×10⁷ | 0.588051475×10⁶ | -0.157373466×10⁸ | 0.276671733×10⁹ | -0.217615510×10¹⁰ | 0.67121314×10¹¹ |
| 6        | 0.874218483×10⁻⁴ | -0.104397770×10⁻⁴ | 0.847564491×10⁶ | -0.147034346×10⁷ | 0.931407805×10⁶ | -0.280229117×10⁸ | 0.439017141×10⁹ | -0.333951526×10¹⁰ | 0.10101504⁰×10¹¹ |
| 7        | 0.130576767×10⁻⁴ | -0.107990536×10⁻⁴ | 0.164275799×10⁶ | -0.169491618×10⁶ | 0.867333556×10⁷ | -0.237176821×10⁸ | 0.350098632×10⁹ | -0.262305852×10¹⁰ | 0.781247654×10¹¹ |
| 8        | 0.206886625×10⁻⁴ | -0.111130885×10⁻⁴ | 0.16151618×10³ | -0.169828586×10⁶ | 0.933477114×10⁶ | -0.266842429×10⁹ | 0.40449322×10¹⁰ | -0.308099132×10¹⁰ | 0.927053336×10¹¹ |
| 9        | 0.323544041×10⁻⁴ | -0.11480459×10⁻⁴ | 0.190230296×10⁶ | -0.27758879×10⁷ | 0.167583964×10⁶ | -0.488514291×10⁹ | 0.739258454×10⁹ | -0.559128198×10¹⁰ | 0.166941689×10¹¹ |
| 10       | 0.474515404×10⁻⁴ | -0.120225797×10⁻⁴ | 0.320379287×10⁶ | -0.24284906×10⁷ | 0.893135217×10⁷ | -0.18956820×10⁸ | 0.287461583×10⁹ | -0.16198316×10¹⁰ | 0.452761220×10¹¹ |
| 11       | 0.439397909×10⁻⁴ | -0.119224343×10⁻⁴ | 0.177276579×10³ | -0.23918085×10⁶ | 0.15386621×10⁷ | -0.3841218×10⁹ | 0.563259564×10⁸ | -0.418763098×10¹⁰ | 0.12346143⁰×10¹¹ |
| 12       | 0.246800711×10⁻⁴ | -0.11358321×10⁻⁴ | 0.210755163×10⁶ | -0.26766526×10⁷ | 0.148126308×10⁷ | -0.41269275×10⁹ | 0.608552008×10⁸ | -0.45284813⁰×10¹³ | 0.13372284⁰×10¹³ |
Table A5. Parameters used in Eq. (A.4) for the DR rate coefficients of BeH+ displayed in Fig. 8.

| \( v_i \) | \( A_{v_i} \) | \( n_{v_i} \) | \( B_{v_i} \) | \( B_{v_i} \) | \( B_{v_i} \) | \( B_{v_i} \) | \( B_{v_i} \) | \( B_{v_i} \) |
|-------|----------|----------|----------|----------|----------|----------|----------|----------|
| 0     | 2.053511320 \times 10^{-9} | 0.592469479 | -0.190649410 \times 10^7 | 0.123315004 \times 10^7 | -0.388342503 \times 10^9 | 0.647265585 \times 10^{11} | -0.566722264 \times 10^{13} | 0.232698887 \times 10^{15} | -0.295078806 \times 10^{16} |
| 1     | 0.314462330 \times 10^{-5} | -0.407538250 | 0.958577714 \times 10^3 | 0.325496198 \times 10^5 | -0.192640935 \times 10^{11} | 0.271812541 \times 10^{13} | -0.194765342 \times 10^{15} | 0.557221814 \times 10^{17} |
| 2     | 0.114678715 \times 10^{-5} | -0.323376187 | -0.265630394 \times 10^3 | 0.219601686 \times 10^6 | 0.207235186 \times 10^{11} | -0.259613563 \times 10^{13} | 0.169369674 \times 10^{15} | -0.449074035 \times 10^{17} |
| 3     | 0.849641548 \times 10^{-6} | -0.275140774 | 0.171673851 \times 10^3 | -0.451956583 \times 10^6 | 0.285086525 \times 10^{13} | -0.827403486 \times 10^{15} | 0.123588775 \times 10^{17} | -0.921680323 \times 10^{19} | 0.271412346 \times 10^{21} |
\[
\frac{v_i}{v_f} \quad A_{i+1} + B_{f} \rightarrow A_{i} + B_{f+1} (1)
\]

Table A6. Parameters for the VE and VIE coefficients of B+H (\(v_i = 0\) and 1). Fig. 8.
### Table A7: Parameters for the VE and VIE rate coefficients of BH$_{2}$ ($r_{+}$ = 2 and 3) from Fig. 8.

| $\alpha_{+}^{i}$ | $A_{+}^{i}$ | $B_{+}^{i}$ | $C_{+}^{i}$ | $D_{+}^{i}$ | $E_{+}^{i}$ | $F_{+}^{i}$ | $G_{+}^{i}$ | $H_{+}^{i}$ | $I_{+}^{i}$ |
|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 0.000            | -0.722      | 0.722       | 0.446       | -0.446      | -0.293      | 0.293       | -0.166      | 0.166       | -0.166      |
| 0.001            | -0.722      | 0.722       | 0.446       | -0.446      | -0.293      | 0.293       | -0.166      | 0.166       | -0.166      |
| 0.002            | -0.722      | 0.722       | 0.446       | -0.446      | -0.293      | 0.293       | -0.166      | 0.166       | -0.166      |
| 0.003            | -0.722      | 0.722       | 0.446       | -0.446      | -0.293      | 0.293       | -0.166      | 0.166       | -0.166      |

Note: The table continues with similar entries for various values of $\alpha_{+}^{i}$.
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