Electron–molecular cation reactive collisions: from channel mixing to competitive processes

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1. Introduction

Dissociative recombination (DR) of molecular cations with electrons [1, 2]:

\[ \text{AB}^+ (N_i^+, v_i^+) + e^{-}(\varepsilon) \rightarrow [A + B]_\varepsilon \] (1)

is one of the simplest reactive collisions; it drives the charged particle densities in astrophysical ionized media, fusion plasmas in the divertor region, hypersonic entry plasmas and in many other cold media of technological interest [3, 4]. Eq. (1) is appropriate for diatomic systems, but can be generalized for polyatomic ones: \( N_i^+ \) and \( v_i^+ \) stand for the initial rotational and vibrational quantum number in the relevant modes of the target cation, considered in its ground electronic state, \( \varepsilon \) for the energy of the incident electron and \( \varepsilon \) for the relative kinetic energy release of the products. During the last 60 years, DR has been the subject of an increasing number of experimental and theoretical studies. However, this process is just one among several reactions triggered by the electron impact on molecular cations. Indeed, elastic, inelastic or superelastic
electron scattering:

\[ AB^+(N_i^+, v_i^+) + e^-(\varepsilon_i) \rightarrow AB^+(N_f^+, v_f^+) + e^-(\varepsilon_f) \]  

(2)

corresponding to \( \varepsilon_f \) equal, smaller or larger than \( \varepsilon_i \) respectively, and, if \( \varepsilon_i \) exceeds the dissociation energy of the target cation, electron impact ion dissociation, i.e. dissociative excitation:

\[ AB^+(N_i^+, v_i^+) + e^-(\varepsilon_i) \rightarrow [A + B^+]_{(e)} + e^-(\varepsilon_f) \]  

(3)

strongly compete with DR. These are also very important processes for the chemistry and for the energetics of the molecular species in cold reactive media.

In this article, after highlighting the major elements of the theoretical background (section 2), we will address some of these processes starting from the simplest mechanisms and advancing towards the complex ones (section 3), illustrating our approach with concrete results on the HD\(^+\)/HD and CO\(^+\)/CO systems. Section 4 will provide our conclusions and perspectives.

2. Theoretical Background

During the processes (1, 2, 3), intermediate collision complexes in so-called super excited states are formed, and their account allows the writing of the preceding reactions in the global form:

\[ AB^+(N_i^+, v_i^+) + e^-(\varepsilon) \rightarrow AB^*, AB^{*(c)}, AB**, AB^{**(c)} \rightarrow \text{products, energy} \]  

(4)

in which \( AB^* \) stands for states bound from both electronic and vibrational point of view, \( AB^{*(c)} \) for states from the mono-electronic continuum (superscript \( (c) \)), \( AB^* \) for states bound from the electronic point of view but dissociative (i.e. from the vibrational continuum), and \( AB^{**(c)} \) for states from the mono-electronic continuum and dissociative. The occurrence of \( AB^* \) states, often called 'Rydberg resonances', is the main reason for the building of an approach of the DR [5, 6, 7, 8, 9] based on the Multichannel Quantum Defect Theory (MQDT) [10, 11, 12, 13]. The processes (1-3) 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 [6, 7, 14], an ionization channel is built starting from the ground electronic state of the ion in one of its ro-vibrational levels \( N^+v^+ \), and is completed by gathering all the mono-electronic states of a given orbital quantum number \( l \), describing an 'optical' electron. These mono-electronic states describe, with respect to the \( N^+v^+ \) threshold, either a 'free' electron - in which case the total state \( AB^{*(c)} \) corresponds to (auto)ionization - or to a bound one - in which case the total state \( AB^* \) corresponds to a temporary capture into a Rydberg state. Meanwhile, a dissociation channel relies on an electronically bound state \( AB^{**(c)} \) whose potential energy in the asymptotic limit is situated below the total energy of the system.

Accordingly, the ionization channels gather together \( AB^* \) and \( AB^{*(c)} \) states, and the dissociation channels correspond to \( AB^{**(c)} \) states. As for those of \( AB^{**(c)} \) type, they can be organized 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 fragmentation 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. The inclusion of the closed channels - including \( AB^* \) states - allows for the indirect mechanism, which interferes with the direct one resulting in the total process.

Our MQDT approach starts with the building of the interaction matrix \( \mathbf{V} \), performed in the ‘A-region’ [15], 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 \( \mu^A_i \), 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, \( V^{(e)A}_{d_j} \), 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 \( V \):

\[
V^{NMA}_{d_j,lN^+v^+}(E, E) = \langle \chi^A_{d_j} | V^{(e)A}_{d_j,l} | \chi^A_{N^+,v^+} \rangle
\]

where \( E \) is the total energy and \( \chi^A_{d_j} \) and \( \chi^A_{N^+,v^+} \) 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 \( V \) and from the zero-order Hamiltonian \( H_0 \), we build the reaction \( K \)-matrix, which satisfies the Lippmann-Schwinger equation [16]:

\[
K = \mathcal{V} + \frac{1}{E - H_0} \mathcal{K}
\]

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 \( K \):

\[
K U = -\frac{1}{\pi} \tan(\eta) U
\]

In the external ‘B-region’ [15] the Born-Oppenheimer model is no longer valid for the neutral molecule, and a frame transformation [17, 18, 19] is performed, via the projection coefficients:

\[
C_{lN^+v^+,\Lambda_\alpha} = \left( \frac{2N^++1}{2N^+} \right)^{1/2} (l (\Lambda - \Lambda^+) N^+ N^+ (l N^+ N\Lambda) \\
\times \left[ 1 + r(r-1)N-1-N^+ \right] \frac{1}{2(\pm,\pm,\pm,\pm)l} \sum_{\alpha} U^\Lambda_{l_{\alpha},\alpha} (\chi^A_{N^+,v^+} | \chi^N_{Nv})
\]

\[
C_{d_j,\Lambda_\alpha} = U^\Lambda_{d_j,\alpha} \cos \eta^\Lambda_{d_j,\alpha}
\]

which can be represented by matrix \( C \). The other solutions, represented by matrix \( S \), are obtained as \( S_{lN^+v^+,\Lambda_\alpha} \) and \( S_{d_j,\Lambda_\alpha} \) by replacing cosine with sine in Eqs. (8) and (9). In the equations, \( \chi^N_{Nv} \) is the vibrational wavefunction of the neutral system in the interaction (A) region. The quantities \( r^\pm \) and \( r \) 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:

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

Imposing boundary conditions leads to the physical scattering matrix [10]:

3
\[ S = X_{oo} - X_{oc} \frac{1}{X_{cc} - \exp(-i2\pi\nu)} X_{co} \]  

(11)

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

For a molecular ion initially on the level \( N_i v_i^+ \) recombining with an electron of energy \( \varepsilon \), the cross section of capture into all the dissociative states \( d_j \) of the same symmetry can be written:

\[ \sigma_{\text{sym}, \text{diss}}^{N_i v_i^+} = \frac{\pi}{4\varepsilon} \frac{2N_i + 1}{2N_i + 1} \rho_{\text{sym}} \sum_{l, j} |S_{d_j l N_i v_i^+}^N|^2 \]  

(12)

Here \( \rho_{\text{sym}} \) is the ratio between the multiplicities of the neutral and the target ion.

3. Illustrations with new results

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.

In the present work, we will restrict ourselves to the non-rotational case, when rotational excitation and rotational couplings are neglected. In this case, 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 equations (5, 8, 9, 12) become:

\[ \mathcal{V}_{d_j l v^+}^\Lambda (E, E) = \langle \xi_{d_j}^\Lambda | V_{l v^+}^{(e)} | \chi_{v^+} \rangle \]  

(13)

\[ C_{l v^+, \Lambda \alpha} = \sum_v U_{l v^+, \alpha}^\Lambda \langle \chi_{v^+} (R) | \cos(\pi \mu_\alpha^\Lambda (R) + \eta_\alpha^\Lambda) | \chi_v (R) \rangle \]  

\[ C_{d v^+, \Lambda \alpha} = U_{d v^+, \alpha}^\Lambda \cos \eta_\alpha^\Lambda \]  

(14)

\[ \sigma_{\text{sym}, \text{diss} \leftarrow v_i^+}^\Lambda = \frac{\pi}{4\varepsilon} \rho_{\text{sym}, \Lambda} \sum_{l, j} |S_{d_j l v_i^+}^\Lambda|^2 \]  

\[ \sigma_{\text{sym}, \text{diss} \leftarrow v_i^+}^\Lambda = \sum_{\Lambda} \sigma_{\text{sym}, \text{diss} \leftarrow v_i^+}^\Lambda \]  

(15)
In order to illustrate the concept of open and closed channels, and to be more specific, we address the case of the HD$^+/\text{HD}$ system, for which a relevant energy diagram - restricted to the $^1\Sigma^+_g$ symmetry of the neutral - is given in Figure 1. 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 ($v^+=0$). This channel, gathering together states of the type HD$^+(c)$ (according to section 2), and the dissociative channel, consisting on the state HD$^{**}$, are always open; all the other channels, which are of ionization type, associated to $v^+=1, 2, \text{etc}$, are closed, and correspond to families of states of the type HD$^*$. A Born-Oppenheimer - and therefore, approximate - picture of some of these states, i.e. those labelled by $^1\Sigma^+_g(1s\sigma_g5s\sigma_g)$, $v=0, 1, 2, \text{etc}$, is shown in green in Figure 1. $E_2$ represents a total energy for which ionization channels associated to $v^+\geq 8$ are open, and those associated to $v^+\geq 8$ are closed.

3.1. The direct process at low energy: recombination versus vibrational (de-)excitation

When the closed channels are either not available or neglected, the $X$-matrix from eq. (10) reduces to its $X_{oo}$ component and all the resonant part from the second term of the $S$-matrix (eq. (11)) is missing. In the case when (i) one single dissociation channel ‘$d$’ is open only, (ii) the first order solution of the Lippman-Schwinger equation (6) is adopted, and (iii) the R-dependence of the quantum defects is neglected, the direct DR cross section can be written as a product of a capture cross section $\sigma^{(\text{cap})}_{dv_i^+}$ and a ‘survival’ factor $f^{(\text{surv})}_{dv_i^+}$ [7]:

$$
\sigma_{dv_i^+} = \sigma^{(\text{cap})}_{dv_i^+} \cdot f^{(\text{surv})}_{dv_i^+}
$$

$$
\sigma^{(\text{cap})}_{dv_i^+} = \frac{\pi}{\xi} \rho^{\text{sym}} \xi_{v_i^+}^2 \cdot f^{(\text{surv})}_{dv_i^+} = \frac{1}{1 + \sum_{v^+} \xi_{v^+}^2} \left(1 + \sum_{v^+} \xi_{v^+}^2\right)^2
$$

These quantities rely all on the strength of the Rydberg-valence interaction:

$$
\xi_{v^+}^2 = \sum_l \xi_{v^+l}^2 \quad \xi_{v^+l} = \pi \cdot V_{dLv^+}^{\Lambda}
$$
Note that even if we do not use approximations (ii) and (iii) invoked above, the computed direct cross section is very close to that modeled by the simple formulas (16). Figure 2 displays the cross section for DR of a ground state HD$^+$ ion into HD** $^1\Sigma_g^+(2p\sigma_u^2)$ dissociative state in three cases. The simplest one comes from the account of only a single ionization channel, the entrance one, i.e. $v^+ = 0$. DR here is in competition with elastic scattering only and, according to the preceding equations, one finds the cross section given by the smooth black curve in Fig. 2. In a second case, we involve further ionization channels, which means that we allow for more autoionization through vibrational excitation. At very low energy the cross section – the blue curve in Fig. 2 – evolves smoothly, and is identical to that from the first case invoked. However, it drops suddenly as each new vibrational threshold opens, in agreement with the simple predictive formulas (16). When the last vibrational (bound) level is reached ($v^+ = 20$), the cross section continues to decrease without displaying any further step-like structure. Note that autoionization through vibrational excitation results in the decrease of the DR cross section by a factor of up to 5 with respect to the first case discussed.

3.2. The direct process at high energy: recombination versus dissociative excitation

![Figure 3](image-url)

**Figure 3.** Dissociative recombination of $^2\Sigma_g^+(1s\sigma_g)\ v_i^+=0$ HD$^+$ ion. Blue (upper)/red (lower) curves: dissociative excitation neglected/accounted, dashed/continuous corresponding to first-order/second-order calculations respectively. Black dot-dashed curve: computation of Takagi [20]. Circles: Tanabe *et al* [21]. Triangles: Al-Khalili *et al* [22].

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). For the two available electronic states of the ionic core, $^2\Sigma_g^+(1s\sigma_g)$ and $^2\Sigma_u^+(2p\sigma_u)$, we have discretized their vibrational continua by adding a 15 eV high potential energy step at $R=25\ a_0$. This corresponds, for every partial wave of the incident electron, to 334 further ionization channels for the ground core (responsible for what we call DE of the first kind, DE1, relying on states of AB$^4(c)$ type), and to 382 ionization channels for the excited core (responsible for what we call DE of the second kind, DE2, relying on states of AB$^{4(c)}$ type). The red curve in Figure 2 represents the cross section of DR assisted by DE1 only, and shows that this process decreases it with respect to that affected by vibrational excitation (blue curve) by a factor up to 2. We have performed extensive calculations of DE-assisted DR
cross section for capture into all the dissociative states within all the relevant symmetries, \(1\Sigma^+_u\), \(1,3\Sigma^+_u\), \(1,3\Pi_{u,g}\), and for a broad range of energy, 0 – 12 eV. The computations have been carried out in the first and second order of the K-matrix, and relied on molecular data previously used [9, 23, 24]. Our final best result, the full red curve in Figure 3, is in reasonable agreement with previous theoretical estimations [20] and storage-ring measurements [21, 22].

3.3. The indirect process: quantum interference between direct dissociation and temporary capture into bound Rydberg states

![Figure 4. Dissociative Recombination of ground state CO\(^+\). Blue full curve: MQDT total (direct and indirect) cross section [25]. Black/green dots: merged beam [33]/ storage ring [34] results respectively.](image)

As shown in Section 2, allowing for closed channels means taking into account the temporary capture into bound electron-ion states, which induce local resonances in the shape of the cross section, according to Eq. (11). In a Born-Oppenheimer picture, this corresponds to the capture into a Rydberg bound state. 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, which suggests the occurrence of resonant features in the cross section close to these total energies. Since numerous computations of the total - i.e. direct and indirect - process are nowadays available [9], we prefer to illustrate this quantum interference mechanism on the recently studied CO\(^+\)/CO system. This is done in Figure 4, which is based on a number of previous molecular structure calculations [26, 27, 28, 29, 30, 31, 32]. The MQDT cross section displayed in this figure comes from the account of \(1\Sigma^+_u\), \(1\Pi\) and \(3\Pi\) symmetries of CO. For each symmetry, the four lowest dissociative states have been included. The very rich resonant structure covers the range of the measured cross sections obtained in merged-beam [33] and storage ring [34] experiments. According to the authors of ref. [34], the possible presence of ions in the electronically excited A \(^2\Pi\) state in the merged-beam device of ref. [33] might explain the observed discrepancy between the two measurements. However, the average theoretical cross section is found lower than these observations.

4. Conclusion and perspectives
Using the Multichannel Quantum Defect Theory, we have illustrated the competition between different processes, subject to quantum interference: dissociative recombination, vibrational...
excitation, dissociative excitation and resonant capture into super-excited bound states. Dissociative excitation has been included in our approach after extending our collision formalism to the case of two active electronic states of the cation. The computed cross sections for HD⁺/HD and CO⁺/CO systems are in good agreement with the measurements. A huge amount of cross sections and rate coefficients [25, 35, 36] will complete those already displayed in the present article, corresponding to a broad range of energy and coming from careful state-to-state analysis.

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