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

O. Motapon^{1,2}, D. Backodissa², F. O. Waffeu Tamo^{1,2,3},
D. Tudorache⁴, K. Chakrabarti^{2,5}, J. Zs. Mezei^{2,*}, F. Lique^{2,3},
A. Bultel⁷, L. Tchang-Brillet³, O. Dulieu⁶, J. Tennyson⁸, A. Wolf⁹,
X. Urbain¹⁰, and I. F. Schneider^{2,*}

¹Physics Department, University of Douala, P. O. Box 24157, Douala, Cameroon

²LOMC CNRS-FRE-3102, Université du Havre, 76058 Le Havre, France

³LERMA CNRS-UMR-8112, Observatoire de Paris, 92195 Meudon, France

⁴Laboratoire EM2C, CNRS UPR288, École Centrale Paris, 92295 Châtenay-Malabry, France

⁵Dept. of Mathematics, Scottish Church College, 1 & 3 Urquhart Sq., Kolkata 700 006, India

⁶Laboratoire Aimé-Cotton CNRS-UPR-3321, Université Paris-Sud, F-91405 Orsay, France

⁷CORIA CNRS-UMR-6614, Université de Rouen, F-76801 Saint-Etienne du Rouvray, France

⁸Dept. of Physics and Astronomy, University College London, London WC1E 6BT, UK

⁹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, D-69117 Heidelberg, Germany

¹⁰Institute of Condensed Matter and Nanosciences, PAMO - Louvain-la-Neuve, Belgium

*Part of this work has been performed while IFS and JZsM were visitors of Laboratoire Aimé–Cotton, Université Paris-Sud

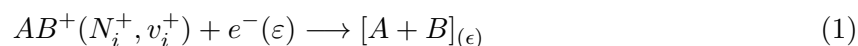
E-mail: ioan.schneider@univ-lehavre.fr

Abstract.

The competition between dissociative recombination, vibrational excitation, and dissociative excitation of molecular cations in electron-impact collisions is discussed within the formalism of the Multichannel Quantum Defect Theory. Illustrative results are given for the HD⁺/HD and CO⁺/CO systems.

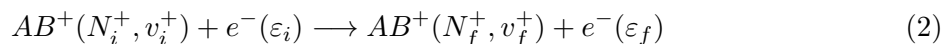
1. Introduction

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

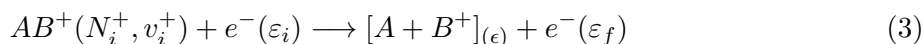


is one of the simplest reactive collisions; it drives the charged particle densities in astrophysical ionized media, fusion plasmas in the divertor region, hypersonic entry plasmas and in many other cold media of technological interest [3, 4]. Eq. (1) is appropriate for diatomic systems, but can be generalized 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, ε for the energy of the incident electron and ϵ 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:



corresponding to ε_f equal, smaller or larger than ε_i respectively, and, if ε_i exceeds the dissociation energy of the target cation, electron impact ion dissociation, i.e. dissociative excitation:



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:



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-adiabatic* 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** 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** 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 \mathcal{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 Λ , 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 μ_l^Λ , 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, $V_{d_j,l}^{(e)\Lambda}$, 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 \mathcal{V} :

$$\mathcal{V}_{d_j, lN^{+v+}}^{NM\Lambda}(E, E) = \langle \chi_{Nd_j}^\Lambda | V_{d_j,l}^{(e)\Lambda} | \chi_{N^{+v+}}^\Lambda \rangle \quad (5)$$

where E is the total energy and $\chi_{d_j}^\Lambda$ and $\chi_{N^{+v+}}^\Lambda$ are the nuclear wave-functions corresponding to a dissociative state and to an ionization channel, respectively. This procedure applies in each Λ -subspace, and results in a block-diagonal global interaction matrix.

Starting from the interaction matrix \mathcal{V} and from the zero-order Hamiltonian \mathbf{H}_0 , we build the reaction K-matrix, which satisfies the Lippmann-Schwinger equation [16]:

$$\mathcal{K} = \mathcal{V} + \mathcal{V} \frac{1}{E - \mathbf{H}_0} \mathcal{K} \quad (6)$$

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 \mathcal{K} :

$$\mathcal{K}\mathbf{U} = -\frac{1}{\pi} \tan(\eta)\mathbf{U} \quad (7)$$

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:

$$\begin{aligned} \mathcal{C}_{lN^{+v+}, \Lambda\alpha} &= \left(\frac{2N^{+1}+1}{2N+1} \right)^{1/2} \langle l(\Lambda - \Lambda^+) N^+ \Lambda^+ | lN^+ N\Lambda \rangle \\ &\times \frac{1+\tau^+\tau(-1)^{N-l-N^+}}{[2(2-\delta_{\Lambda^+,0})(1+\delta_{\Lambda^+,0}\delta_{\Lambda,0})]^{1/2}} \times \sum_v U_{lv,\alpha}^\Lambda \langle \chi_{N^{+v+}}^{\Lambda^+} | \cos(\pi\mu_l^\Lambda(R) + \eta_\alpha^\Lambda) | \chi_{N^v}^\Lambda \rangle \end{aligned} \quad (8)$$

$$\mathcal{C}_{d_j, \Lambda\alpha} = U_{d_j\alpha}^\Lambda \cos \eta_\alpha^\Lambda \quad (9)$$

which can be represented by matrix \mathcal{C} . The other solutions, represented by matrix \mathcal{S} , are obtained as $\mathcal{S}_{lN^{+v+}, \Lambda\alpha}$ and $\mathcal{S}_{d_j, \Lambda\alpha}$ by replacing cosine with sine in Eqs. (8) and (9). In the equations, $\chi_{N^v}^\Lambda$ is the vibrational wavefunction of the neutral system in the interaction (A) region. The quantities τ^+ and τ 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 \mathcal{C} and \mathcal{S} are the building blocks of the generalized scattering matrix \mathbf{X} , involving all the channels, open ('o') and closed ('c'), and organized in 4 sub-matrices:

$$\mathbf{X} = \frac{\mathcal{C} + i\mathcal{S}}{\mathcal{C} - i\mathcal{S}} \quad \mathbf{X} = \begin{pmatrix} \mathbf{X}_{oo} & \mathbf{X}_{oc} \\ \mathbf{X}_{co} & \mathbf{X}_{cc} \end{pmatrix} \quad (10)$$

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

$$\mathbf{S} = \mathbf{X}_{oo} - \mathbf{X}_{oc} \frac{1}{\mathbf{X}_{cc} - \exp(-i2\pi\boldsymbol{\nu})} \mathbf{X}_{co} \quad (11)$$

where the diagonal matrix $\boldsymbol{\nu}$ 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 labelling a *closed* channel).

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

$$\sigma_{diss \leftarrow N_i^+ v_i^+}^{N, sym} = \frac{\pi}{4\varepsilon} \frac{2N+1}{2N_i^++1} \rho^{sym} \sum_{l, \Lambda, j} |S_{d_j, l N_i^+ v_i^+}^{N \Lambda}|^2 \quad (12)$$

Here ρ^{sym} is the ratio between the multiplicities of the neutral and the target ion.

3. Illustrations with new results

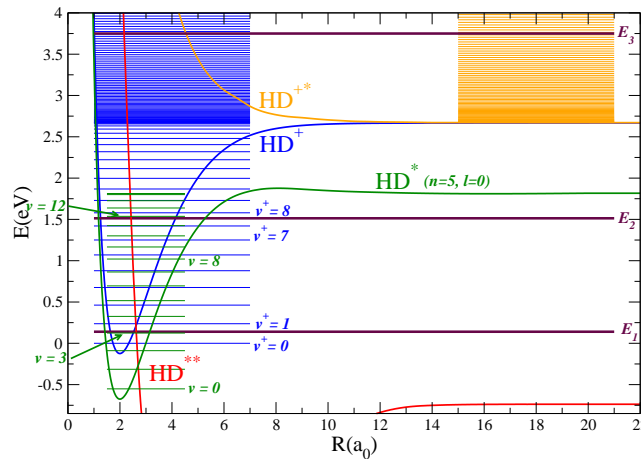


Figure 1. HD⁺/HD states (potential energy curves and vibrational levels) relevant for the electron/HD⁺ reactive collisions: HD⁺ ²Σ_g⁺(1sσ_g) (blue), HD⁺ ²Σ_u⁺(2pσ_u) (orange), HD** ¹Σ_g⁺(2pσ_u²) dissociative state (red), and HD* ¹Σ_g⁺(1sσ_g, 5sσ_g) Rydberg state (green). The violet lines represent illustrative 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 Λ and eventually sum over this quantum number the resulting cross sections. For a given Λ , the equations (5, 8, 9,12) become:

$$\mathcal{V}_{d_j, l v^+}^{\Lambda}(E, E) = \langle \chi_{d_j}^{\Lambda} | V_{d_j, l}^{(e)\Lambda} | \chi_{v^+} \rangle \quad (13)$$

$$\mathcal{C}_{l v^+, \Lambda \alpha} = \sum_v U_{l v, \alpha}^{\Lambda} \langle \chi_{v^+}(R) | \cos(\pi \mu_l^{\Lambda}(R) + \eta_{\alpha}^{\Lambda}) | \chi_v(R) \rangle \quad \mathcal{C}_{d, \Lambda \alpha} = U_{d \alpha}^{\Lambda} \cos \eta_{\alpha}^{\Lambda} \quad (14)$$

$$\sigma_{diss \leftarrow v_i^+}^{sym, \Lambda} = \frac{\pi}{4\varepsilon} \rho^{sym, \Lambda} \sum_{l, j} |S_{d_j, l v_i^+}^{\Lambda}|^2 \quad \sigma_{diss \leftarrow v_i^+}^{sym} = \sum_{\Lambda} \sigma_{diss \leftarrow v_i^+}^{sym, \Lambda} \quad (15)$$

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. 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 $\text{HD}^{*(e)}$ (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 $v^+=1, 2$, 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 $^1\Sigma_g^+(1s\sigma_g 5s\sigma_g)$, $v=0, 1, 2$, etc., 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.

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

When the closed channels are either not available or neglected, the \mathbf{X} -matrix from eq. (10) reduces to its \mathbf{X}_{oo} component and all the resonant part from the second term of the \mathcal{S} -matrix (eq. (11)) is missing. In the case when (i) one single dissociation channel 'd' is open only,

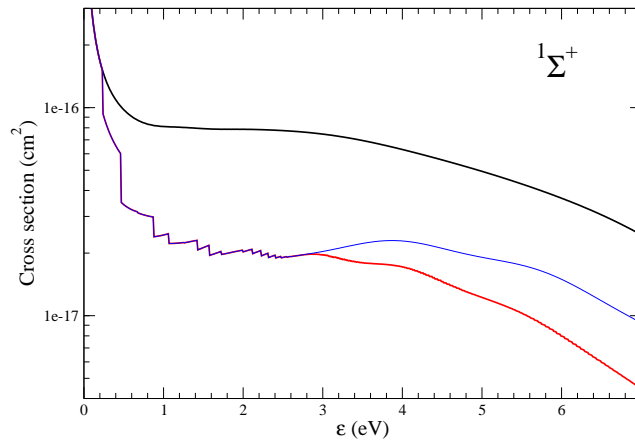


Figure 2. Direct dissociative recombination of $^2\Sigma_g^+(1s\sigma_g) v_i^+=0$ HD^+ ion into $\text{HD}^{**} ^1\Sigma_g^+(2p\sigma_u^2)$ state. Black curve: only $v^+=0$ included in the calculation. Blue curve: all bound vibrational levels ($v^+=0-20$) included. Red curve: bound vibrational levels *and* discretized vibrational levels from the continuum ($v^+=21-355$) included.

(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 $\sigma_{dv_i^+}^{(cap)}$ and a 'survival' factor $f_{dv_i^+}^{(surv)}$ [7]:

$$\sigma_{dv_i^+} = \sigma_{dv_i^+}^{(cap)} \cdot f_{dv_i^+}^{(surv)} \quad \sigma_{dv_i^+}^{(cap)} = \frac{\pi}{\varepsilon} \rho^{sym,\Lambda} \tilde{\xi}_{v_i^+}^2 \quad f_{dv_i^+}^{(surv)} = \frac{1}{[1 + \sum_{v^+} \tilde{\xi}_{v^+}^2]^2} \quad (16)$$

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

$$\tilde{\xi}_{v^+}^2 = \sum_l \xi_{v^+l}^2 \quad \xi_{v^+l} = \pi \cdot \mathcal{V}_{d,lv^+}^\Lambda \quad (17)$$

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 $\text{HD}^{**} \ ^1\Sigma_g^+(2p\sigma_u^2)$ 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

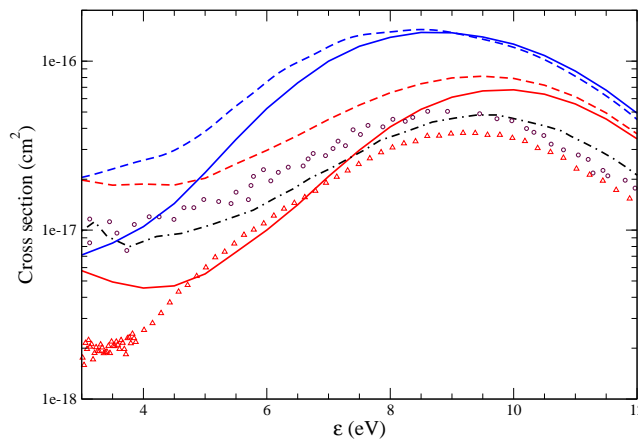


Figure 3. Dissociative recombination of $^2\Sigma_g^+(1s\sigma_g) v_i^+=0$ HD^+ ion. Blue (upper)/red (lower) curves: dissociative excitation neglected/accounted, dashed/continuous corresponding to first-order/second-order calculations respectively. Black dot-dashed curve: computation of Takagi [20]. 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 $\text{AB}^{*(c)}$ 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 $\text{AB}^{** (c)}$ 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, $^1\Sigma_g^+$, $^{1,3}\Sigma_u^+$, $^{1,3}\Pi_{u,g}$, 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

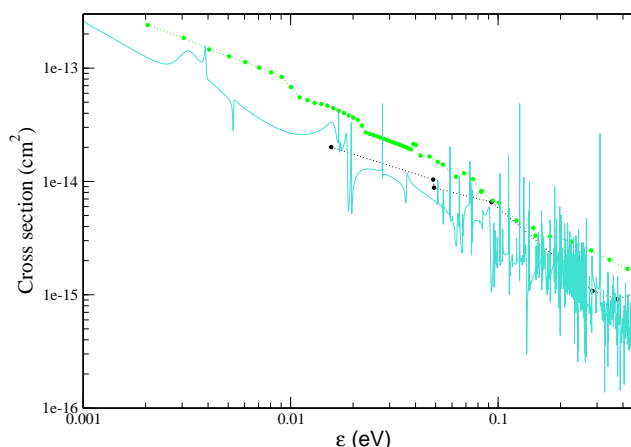


Figure 4. Dissociative Recombination of ground state CO^+ . Blue full curve: MQDT total (direct and indirect) cross section [25]. Black/green dots: merged beam [33]/ storage ring [34] results respectively.

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 $^1\Sigma^+$, $^1\Pi$ 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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