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The role of Rydberg states in dissociative recombination, as revealed by ion storage ring experiments

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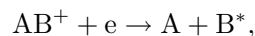
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After a brief presentation of the dissociative recombination process and of the recent measurements performed with ion storage rings by several groups of experimentalists, we analyse the role of Rydberg states in the dynamics of the reaction. They are responsible for various kinds of resonances observed in the experimental cross sections. *Bound* Rydberg states cause narrow resonances, mostly in the form of dips at very low energy (rovibrationally excited Rydberg states with ground state ion core), and of peaks at higher energy (Rydberg states with excited state ion core). At still higher energy (approximately 10 eV and higher) entire series of *dissociative* Rydberg states with repulsive ion core cause very broad (a few eV) composite resonances which dominate the process. Competition with dissociative excitation ($AB^+ + e \rightarrow A + B^+ + e$) must be included in the theoretical treatment above the ion dissociation threshold. Calculations for HD^+ and CD^+ , based on a multichannel quantum defect approach, are described.

1. Introduction

The dissociative recombination (DR) of a molecular ion AB^+



is a reactive process which involves almost all aspects of molecular dynamics: ionization and autoionization; dissociation and predissociation; electronic and rovibrational interactions. In particular, a central role is played by Rydberg states which show up as *resonances* in the experimental cross sections, with different shapes and widths depending on the energy range and on the type of Rydberg state involved. In this paper, we will first present the most recent experimental technique of measurement, using ion storage rings, and review the main features and some theoretical approaches of this process. We will then describe and analyse two experiments which demonstrate the role of Rydberg states as follows.

(1) The first experiment has been performed on the CRYRING storage ring in Stockholm (Strömholm *et al.* 1995) for the molecular ion HD^+ stored for about 25 s before recombining. The electron energy (relative to the ion beam) ranges from 1 meV–20 eV, and two energy regions for the incident electrons will be distinguished in the analysis. At low energy, near the first ionization threshold, rovibrationally excited levels of Rydberg states converging to the ground state ion core are responsible for interferences, mostly destructive, with the direct electron capture into the low-lying $^1\Sigma_g^+$ dissociative state of HD. At much higher energy, above the ion dissociation threshold of HD^+ (approximately 2.7 eV), the major contribution to DR is made by entire series of core-excited *dissociative* Rydberg states of various symmetries.

(2) In the second experiment, performed at the TSR ring in Heidelberg, the DR cross section of CD^+ has been measured (Forck *et al.* 1994) and revealed a new class of Rydberg resonances at intermediate energy (approximately 1 eV), due to core-excited *bound* Rydberg states which interfere constructively with the direct dissociation.

We conclude with a perspective towards future developments, the most important being to study the long-range behaviour of the dissociating flux, in order to predict or explain branching ratios between the various fragmentation channels.

2. A new experimental technique, using ion storage rings

Dissociative recombination is an important process determining the electronic densities and the molecular abundances in the ionosphere and in the interstellar medium. The experimental determination of rate coefficients of use for these very cold and diffuse media is challenging, because they require measurements at *very low collision energy* for *fully relaxed ions* (electronically, vibrationally and rotationally). Both requirements were very difficult to achieve in the traditional experimental techniques (plasmas afterglow, SIFT, crossed or merged beam devices, see, for example, the review by Mitchell (1990)). A new generation of experiments, very promising as a source of astrophysical data, has been developed in recent years (Tanabe *et al.* 1993; Forck *et al.* 1993a; Larsson *et al.* 1993; Schmidt *et al.* 1996). Several experimental groups using ion storage rings to study heavy atomic ions recently turned to store molecular ions (on TARN II in Tokyo, TSR in Heidelberg, CRYRING in Stockholm, ASTRID in Aarhus). The residence time of the ions may reach several seconds, allowing relaxation of all the electronic and (at least for heteronuclear ions with a permanent dipole) vibrational excited states. Additional phase-space cooling is achieved using an electron cooler device, which also provides the recombining electrons. The DR cross section is then measured as a function of the relative velocity between the electron and ion merged beams. As an example, figure 1 shows the device used at CRYRING and the reader can find experimental details in the review papers by Forck *et al.* (1993b) and by Larsson (1995).

The large energy range covered in these new experiments requires several extensions to the theoretical treatments of DR, both in the mechanisms involved and in the number of molecular states to be included in the calculations. The simplest molecular ions H_2^+ , D_2^+ and HD^+ have been extensively studied as test cases. It is crucial to achieve there a good agreement between theory and experiment, in particular to check the efficiency of ion cooling and the calibration of the absolute measurements of the rate coefficients. Then, one will be able to use safely the experimental results for more complex ions, in particular large polyatomic ions, very important for atmospheric or interstellar equilibrium but almost intractable theoretically.

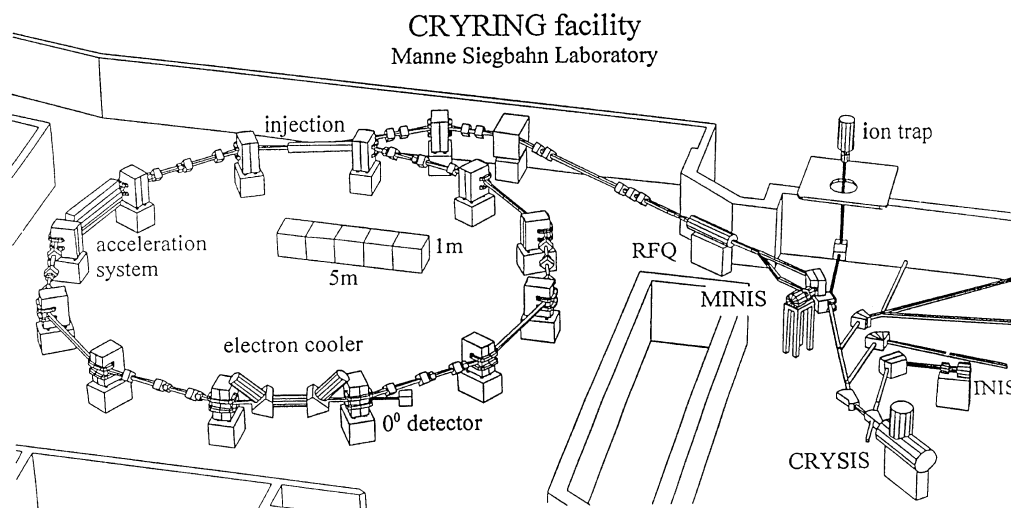


Figure 1. The CRYRING facility at the Manne Siegbahn Laboratory at Stockholm University. The circumference of the ring is 52 m. The electron–ion recombination takes place in the electron cooler, and the DR neutral products are detected in the 0° -detector arm (from Larsson 1995).

3. Mechanisms and theoretical treatment of DR: a brief review

Several review papers describe the basic mechanisms and the main theoretical treatments of dissociative recombination (Giusti-Suzor 1989; Guberman 1993; Takagi 1993; Giusti-Suzor *et al.* 1993), with many references therein. Briefly, dissociative recombination may be viewed as a *multichannel reactive collision* involving two types of ‘channels’: *ionization channels* (electron–molecular ion scattering) on the one hand, an example of which is the entrance channel, and *dissociation channels* (atom–atom scattering) on the other hand. An ionization channel with threshold above the total energy available in a specific recombination process is termed ‘closed’ and introduces in the calculation a series of Rydberg states differing only by the principal quantum number of the external electron. At high energy, some open ionization channels become also dissociative, when the total energy is higher than the ion state dissociation limit. This gives rise to dissociative excitation, a competitive process to dissociative recombination.

Dissociative recombination, as well as associative ionization (the inverse process, see, for example, Weiner *et al.* 1989) results from various couplings between these two types of channels. The dominant interaction is usually the *electronic coupling* between the Rydberg manifold or adjoining ionization continuum (singly excited configurations) and the dissociative valence states (doubly excited configurations) whose potential curves cross the ion ground state in the Franck–Condon region. This interaction allows *direct* electron capture into the dissociative channels, measured by the so-called ‘electronic width’ $\Gamma(R)$, with competing autoionization back to the open ionization channels. Other types of interchannel couplings, the *vibrational* and *rotational* interactions between alternative ionization channels, may cause electron capture into rovibrationally excited Rydberg levels (pertaining to the closed ionization channels), which are then predissociated due to electronic coupling with the same dissociative states as for the direct process previously described. This second process has been termed *indirect* DR (Bardsley 1968), as contrasted to the purely electronic direct one. It is responsible for narrow resonances (mostly in the form of dips) in the DR cross sections, as observed in the merged beam experiments at

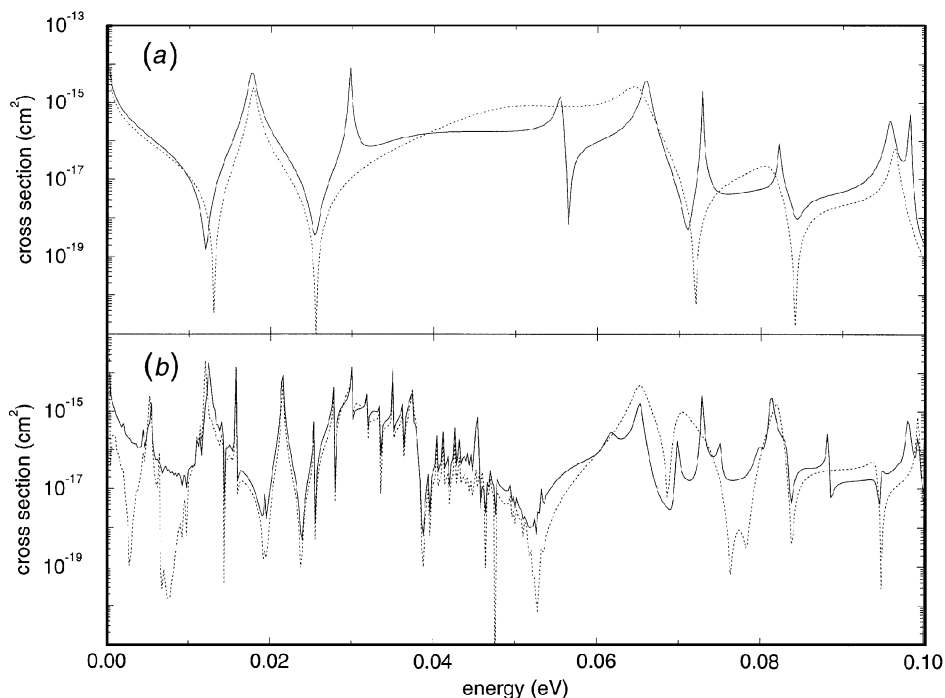


Figure 2. The effect of rotational coupling on the low-energy DR cross section of HD^+ , initially in the lowest rovibrational level of the ground state. The dotted line shows the contribution of the d-wave of the incident electron only, leading to a series of $(1s\sigma_g nd\sigma_g)$ Rydberg resonances, the full line gives the simultaneous contribution of s- and d-waves with the additional $(1s\sigma_g ns\sigma_g)$ Rydberg resonances. (a) Rotational interactions neglected. (b) Rotational interactions included.

low energy (Van der Donk *et al.* 1991). When no doubly excited dissociative state favourably crosses the ion ground state, these rovibronic interactions might nevertheless induce fast DR via low-lying Rydberg states, as for the case of HeH^+ (Guberman 1994; Sarpal *et al.* 1994) and H_3^+ (see § 7a).

The first requirement for a complete study of any DR process is the determination of potential curves (or surfaces) for the dissociative states and the evaluation of their autoionization widths, i.e. of their electronic or non-adiabatic couplings to the entrance ionization channel. Besides using spectroscopic or *ab initio* data in the region of Rydberg-valence states mixing, which may then be extrapolated above the ionization threshold, several methods from electron–molecule scattering theory are used and developed for this step: the *R*-matrix method (Tennyson & Noble 1985; Shimamura *et al.* 1990; Tennyson 1997), the linear algebraic method (Collins *et al.* 1992, 1995), the complex Kohn variational method (Orel *et al.* 1991) and the Ritz variational method with static approximation for the continuum state (Sato & Hara 1986).

In the following we will focus on diatomic molecules where at least one dissociative curve corresponding to a doubly excited state crosses the potential curve of the ion ground state, in a favourable Franck–Condon region. The whole process is thus dominated by strong *electronic* interactions, which induce various resonance structures depending on the energy range. We show below that all these structures are due to Rydberg states, mono- or di-excited, with a bound or dissociative ion core.

4. Low-energy region: rovibrationally excited Rydberg resonances

Only recently did the ion storage rings provide DR cross sections for very slow electrons (1 meV–1 eV), with high enough resolution to show the resonance structure near threshold. In this energy range, below the ion dissociation threshold, electron capture into bound levels of Rydberg mono-excited states induces a typical resonant structure in the cross section, the signature of interferences between the direct and indirect processes. In the case of fast direct DR, due to a low-lying doubly excited dissociative state (e.g. in H_2 and HD) the interferences are mainly destructive in this energy range, leading to dips in the cross section besides small spikes. This results from the nature of the interactions involved: the bound Rydberg states converging to the ion ground state are only coupled by *rovibrational interactions* to the ionization continuum, much weaker than the strong *electronic* coupling leading to direct DR, or to predissociation of the Rydberg states. Note that this does not apply to the ‘non-crossing’ case with no low-lying doubly excited dissociative state (e.g. in HeH and H_3), where rovibrational capture into Rydberg resonances will help DR instead of preventing it.

Most previous DR calculations at low energy, either for H_2^+ (Giusti-Suzor *et al.* 1983; Nakashima *et al.* 1987; Schneider *et al.* 1991, 1994) or for O_2^+ (Guberman & Giusti-Suzor 1991), N_2^+ (Guberman 1991) and CH^+ (Takagi *et al.* 1991), used the two-step MQDT approach (Giusti 1980) with an electronic reaction matrix calculated at first or second order of perturbation. Vibrational couplings among singly excited neutral states were included via the R dependence of the molecular quantum defect, but rotational interactions among Rydberg states of different molecular symmetries were neglected (only rotational initial excitation was considered, together with the corresponding centrifugal distortion of the molecular potential curves). In more recent work on H_2^+ and HD^+ , Takagi included the rotational interactions (Takagi 1993; Tanabe *et al.* 1995) through the same frame transformation as in the original MQDT approach for photoionization (Jungen & Dill 1980). Following a similar approach (but with two Rydberg series— $d\sigma$ and $s\sigma$ —included instead of only $d\sigma$ in Takagi’s calculations) we have performed calculations in the low-energy region for the case of HD^+ initially in its ground vibrational level, taking into account both vibrational and rotational interactions, besides the dominant electronic coupling (Schneider *et al.* 1997). Figure 2 illustrates the increasing complexity of the Rydberg resonance structure, when including the contribution of several electron partial waves (or Rydberg series) and of rotational interactions, besides the electronic and vibrational ones.

Before comparison with the experimental results, two kinds of averaging have to be performed. First, one must average over the velocity distribution in the electron cooler, assumed to be an anisotropic Maxwellian distribution (Larsson 1995). Then, the ion may be initially in various rotational states, since their relaxation time often exceeds the storage time. A separate calculation is performed for each initial rotational level and the final result is obtained by averaging the different cross sections over a Boltzmann distribution of rotational levels corresponding to the room temperature of 300 K. In spite of the large number of resonances due to the rovibrational structure of the Rydberg states, these two averages lead to a relatively smooth cross section, in good agreement with experiments (see figure 3).

5. Intermediate-energy region: core-excited Rydberg resonances

Recent experiments performed on the test storage ring (TSR) in Heidelberg have observed in the DR cross sections of CD^+ (Forck *et al.* 1994), OH^+ (Amitay *et*

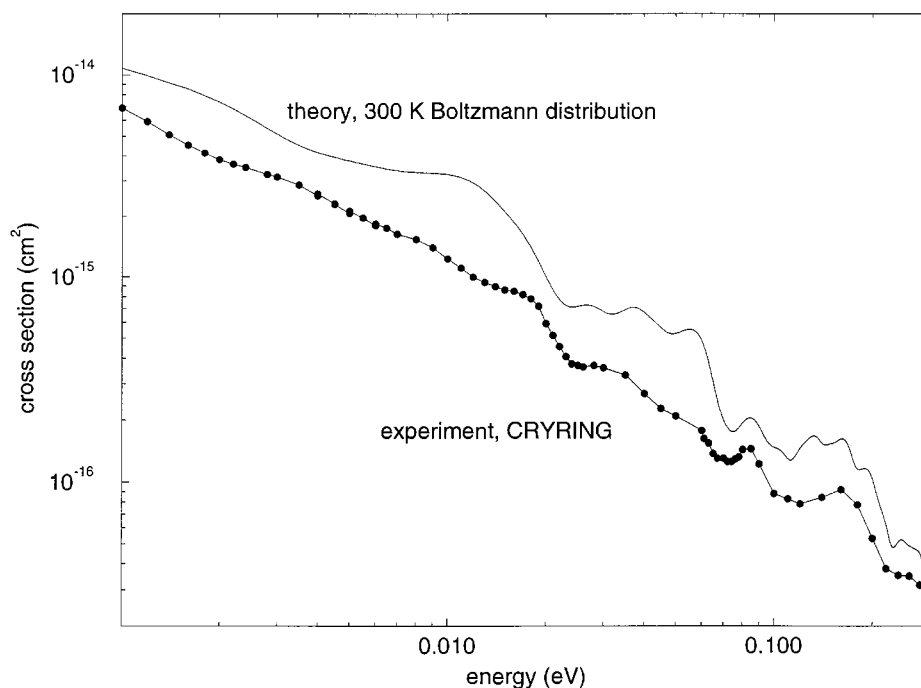


Figure 3. Low-energy cross section for the dissociative recombination of HD^+ . The dots show the absolute cross section as measured at CRYRING (Strömholm *et al.* 1995). The full line represents the $T = 300$ K Boltzmann average of our theoretical results for ion initial levels $v = 0$, $N = 0-10$. The calculations have been performed at second order of the electronic reaction matrix, taking into account the contribution of 'd' and 's' partial waves of the incident electron and simultaneous electronic, vibrational and rotational interactions.

al. 1996a) and CH^+ (Amitay *et al.* 1996b) strong resonances around 1 eV, broader and more prominent than the low-energy resonances discussed above. They could result from a new kind of indirect dissociative recombination process, with temporary capture in core-excited (instead of only vibrationally excited) Rydberg states. Many molecular ions (except for H_2^+ and its isotopomers HD^+ and D_2^+) have low-lying *bound* excited states giving rise to series of bound core-excited Rydberg states in the neutral molecule, e.g. in CH, OH, N_2 . Such doubly excited Rydberg states are electronically coupled both to the initial continuum (incoming electron + ground state ion) and to the dissociative states. They might thus induce these new resonances in the DR cross sections, mostly in the form of peaks due to a strong electronic capture process.

A preliminary study of this mechanism has just been performed in our group (Carata *et al.* 1997) for CD^+ . The MQDT formalism can easily include the core-excited closed channels, as was done previously in molecular photoionization studies to account for electronic autoionization (Giusti-Suzor & Lefebvre-Brion 1980, 1984). The most difficult part is the calculation of the numerous electronic couplings between the different types of channels (Rydberg–Rydberg with different cores, Rydberg–dissociative states). Spectroscopic analysis of molecular spectra can help for this point.

Figure 4b shows the result of a model calculation around 1 eV in CD^+ , where such a prominent resonance has been observed (Forck *et al.* 1994, see figure 4a). Besides the closed ionization channels (or Rydberg series) with the ion ground state in an excited vibrational level as a threshold, we have included in the MQDT treatment

additional closed channels with a bound *electronically excited* ion state as threshold, namely the $a^3\Pi$ ion state with low vibrational quantum number ($v = 0-5$). The ion potential curves and the electronic couplings between mono- and di-excited configurations have been guessed mainly from the CH^+ paper by Takagi *et al.* (1991). A complex resonance structure is obtained in the calculated cross section between 0.6 and 1.2 eV (figure 4b). The broad peak corresponds to the $v = 4$ level of the $[a^3\Pi(4p\sigma)]^2\Pi$ Rydberg state of CD, which interacts electronically both with the ionization continuum of the $X^1\Sigma$ ground state of CD^+ (the entrance channel) and with the lowest dissociative $^2\Pi$ valence state. The narrow resonances on both sides of this relatively broad structure are due to temporary capture (through vibrational interactions) into excited vibrational levels of Rydberg states $[X^1\Sigma(np\pi)]^2\Pi$ with ground state ion core. Such an interfering resonance pattern closely recalls observations reported in photoionization experiments (Dehmer *et al.* 1984) with interfering vibrational and electronic autoionization resonances in the same region of the spectrum. The MQDT approach used to analyse this ‘complex resonance’ feature (Giusti-Suzor & Lefebvre-Brion 1980, 1984) should also lead to a quantitative explanation of the intermediate-energy resonances observed in DR cross sections, in CD^+ or other molecules, once more precise data for the molecular interactions involved (mainly for the electronic couplings) are known.

6. High-energy region: Rydberg series of dissociative states

At still higher energy, above the dissociation limit of the bound ion states, electron capture in bound Rydberg levels is no more possible and DR proceeds through direct electronic recombination into doubly excited dissociative states. More and more dissociative states contribute with increasing energy, and most of them (except for the lowest ones) may be considered as the successive n members of Rydberg series with a given dissociative ion core state and various molecular symmetries. A good picture of this scenario may be found for the case of H_2 in figure 5, where potential curves calculated by Guberman (1983) in a quasi-diabatic approach are represented: two sets of dissociative Rydberg states, the Q_1 states with $2p\sigma_u$ core, and the Q_2 ones with $2p\pi_u$ core, clearly appear below each ion excited state.

These series of dissociative states give rise to very broad resonances in the cross sections, as seen for example in the HD^+ results around 9 eV (Q_1 series) and then about 16 eV (Q_2 series) in different storage ring experiments (Forck *et al.* 1993a; Tanabe *et al.* 1995; Strömholm *et al.* 1995; see figure 6). Similar composite resonances are observed in the HeH^+ measurements of Sundström *et al.* (1994) and Tanabe *et al.* (1993) near 20 eV, and around 10 eV (see figure 4a) in the CD^+ results obtained at TSR by Forck *et al.* (1994). The analysis of this type of resonance is a theoretical challenge: how many dissociative states are involved, of which symmetry?

Here also, the simplest ions H_2^+ , HD^+ and D_2^+ serve as prototypes. MQDT calculations (Strömholm *et al.* 1995; Takagi 1996; Schneider *et al.* 1997) have been performed for the first broad resonance around 9 eV in HD^+ , more suitable for test calculations than the homonuclear isotopomers because of faster vibrational relaxation. It turns out that not only the *lowest* members of each series of dissociative Rydberg states (they have the largest autoionization width which scales as n^{*-3}) but the entire series for each molecular symmetry should be included in order to reproduce the correct *shape* and *magnitude* of the observed composite resonance. This recalls the situation encountered in atomic dielectronic recombination, where entire series of core-excited

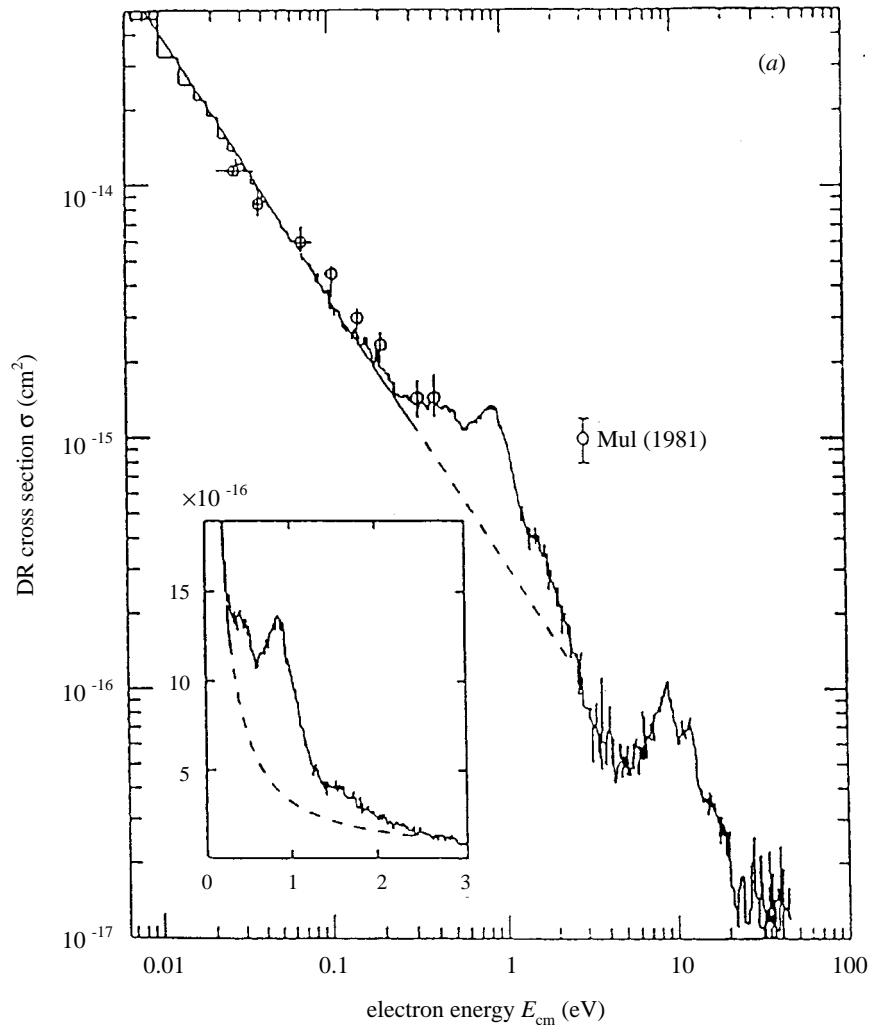


Figure 4. (a) Dissociative recombination cross section of CD^+ measured at TSR by Forck *et al.* (1994) normalized to the results (dots) of Mul *et al.* (1981) (see also Mitchell 1990). The $E^{-0.9}$ dependence of the direct process is indicated by the dashed line, and the inset is a linear scale enlargement of the cross section around the core-excited resonance.

Rydberg states contribute to the broad autoionization resonances observed in the storage ring experiments (see, for example, Kilgus *et al.* 1992).

Unfortunately, *ab initio* structure or collisional calculations become more and more difficult with increasing energy because the electron orbitals involved become very diffuse and large electronic, as well as internuclear, distances must be explored. Precise molecular data are thus lacking except for the lowest members of each series. Extrapolation procedures based on Rydberg-series scaling laws may be used. In particular, the higher members of each series are very close in energy and may be represented by a single effective state with a total width obtained by summing the $n \geq n_0 \approx 6$ individual widths. As an example, figure 6 shows how the contributions of successive- n Rydberg states of a given series add up in the total cross section. Note that dissociative states of the *same symmetry* must be included simultaneously

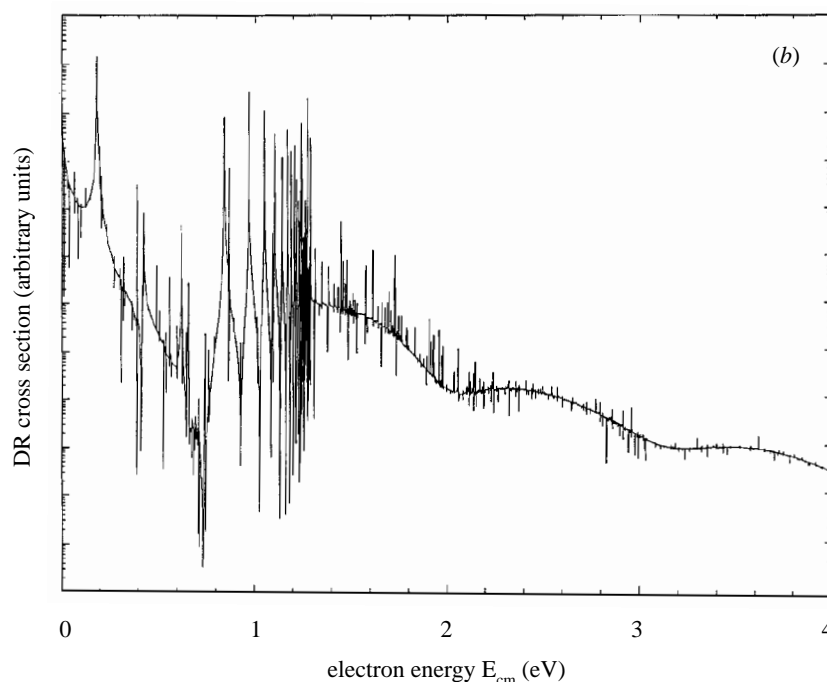
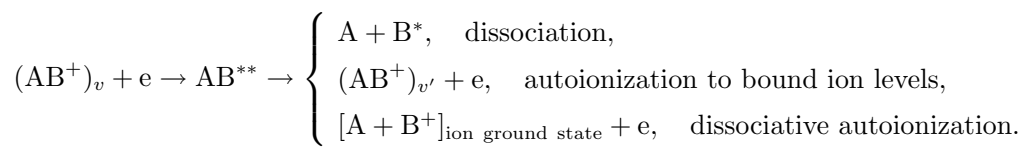


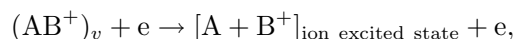
Figure 4. (b) Result of an exploratory MQDT calculation with closed channels (see text) corresponding both to the $X^1\Sigma^+$ and to the $a^3\Pi$ ion cores (Carata *et al.* 1997).

in a single calculation, even if one assumes they are not directly coupled, because they can interact indirectly being coupled to the same set of bound Rydberg states or ionization continuum.

Besides these infinite series of dissociative states, another feature specific to the high-energy region is autoionization into the *vibrational continuum* of the ion ground state, beyond the bound vibrational levels:



At still higher energy the direct *dissociative excitation* process,



also begins to compete with dissociative recombination, as observed in the experiment at TSR on HD^+ (Forck 1994). Closely related to *dissociative photoionization* (see, for example, the recent experiments on H_2 and D_2 by Geddes *et al.* (1994) and Latimer *et al.* (1995)), dissociative excitation and autoionization involve a double continuum (electronic and nuclear) or three-particle fragmentation whose exact treatment requires integration over correlated electron and nuclear kinetic energies. The method proposed by Kanfer & Shapiro (1983) for dissociative photoionization, in which they solve coupled equations for the nuclear motion after having discretized the electronic continuum, could be adapted to dissociative recombination with few changes. Until now, only approximate first-order calculations of dissociative autoionization in HD^+

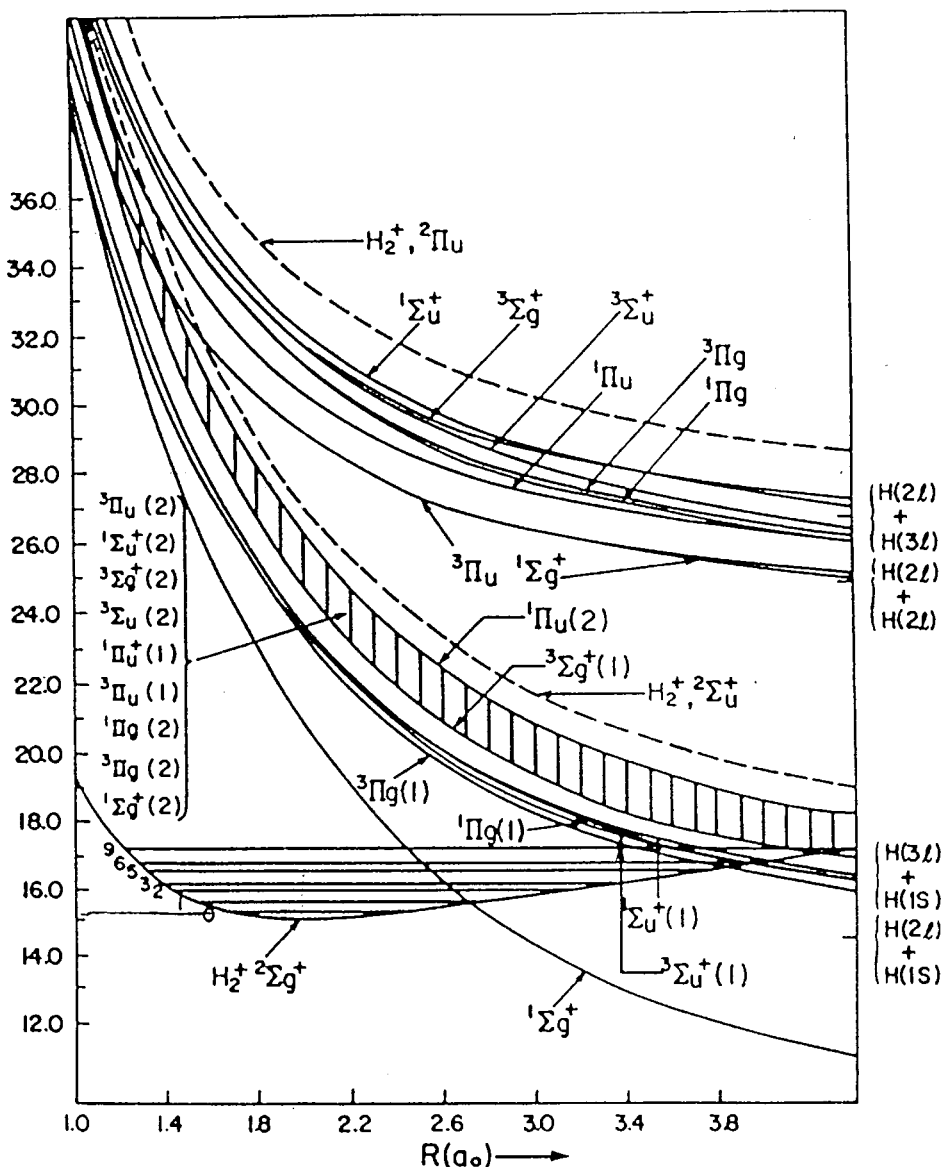


Figure 5. Potential energy curves for H_2 and H_2^+ , from Guberman (1983). The dashed curves correspond to the two first excited states of H_2^+ ($2p\sigma_u$ and $2p\pi_u$), to which many Rydberg series of H_2 dissociative states converge. The same set of electronic states are involved in the dissociative recombination of HD^+ .

have been performed (Strömholm *et al.* 1995; Takagi 1996; Schneider *et al.* 1997) but these preliminary results are, encouragingly, in agreement with the dissociative excitation measurements of Forck (1994). They also lead to DR cross sections, including competitive dissociative autoionization (see figure 7) in good quantitative agreement with the *absolute values* measured on CRYRING (Strömholm *et al.* 1995) in the region of the first broad resonance (approximately 5–13 eV), assuming complete vibrational relaxation of the stored ions. We stress the importance of accurate calculations in this energy range because they can help to calibrate the experimental

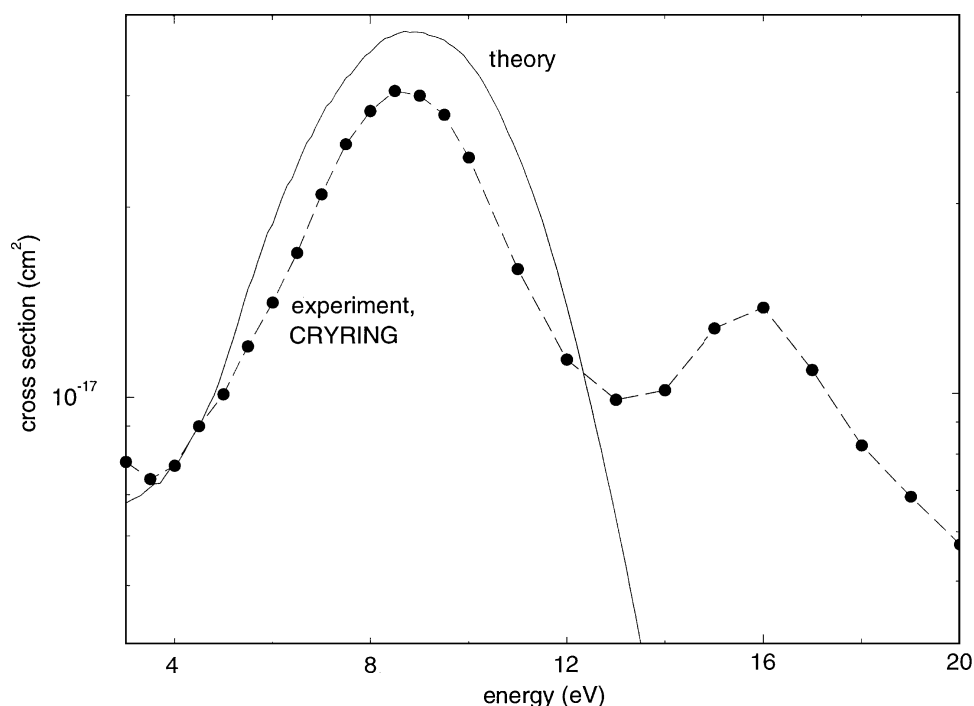


Figure 6. High energy absolute cross section measured for HD^+ at CRYRING by Strömholm *et al.* (1995), compared with the theoretical results of Schneider *et al.* (1997) including all Σ and Π series of dissociative Rydberg states converging to the first excited ($2p\sigma_u$) state of HD^+ .

results, both for absolute values and for the efficiency of internal cooling. Besides the HD^+ case, complete calculations have been recently performed by Orel *et al.* (1995) for HeH^+ in the same high-energy region (10–30 eV), both of the electronic collision and of the multichannel dissociation dynamics, leading to good agreement with the experimental results of Sundström *et al.* (1994).

7. Future

(a) *Dissociative recombination induced by non-adiabatic couplings between Rydberg manifolds*

For several molecular ions (in particular HeH^+ or H_3^+), fast DR rates have been measured near threshold although no dissociative potential curve or surface is known to cross the ion ground state in its Frank–Condon region. The long storage time of the ions in rings alleviates the possibility of fast rates due to excited ion states in the beam. Decisive progress in the analysis has been made recently for the case of HeH^+ by Guberman (1994) using the multichannel quantum defect theory (MQDT) and by Sarpal *et al.* (1994) using the R -matrix approach. Both introduce in their calculations the non-adiabatic radial couplings between electronic states (Rydberg as well as ion + electron continuum) and obtain cross sections, as a result of the breakdown of the Born–Oppenheimer approximation, of the same order of magnitude as the experimental ones although significant differences in resonance structure subsist between both calculations. Extension of these treatments to the polyatomic case, with H_3^+ as first candidate, is one of the most important theoretical developments

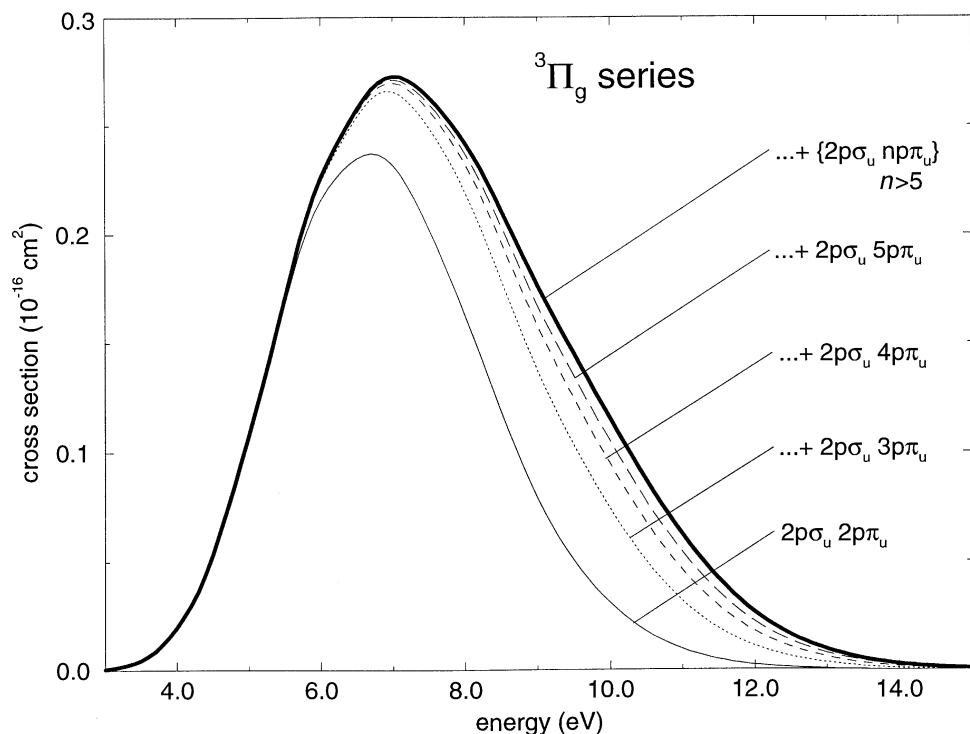


Figure 7. Cumulative contribution of the successive $(2p\sigma_u n p\pi_u)$ ${}^3\Pi_g$ dissociative Rydberg states to HD^+ dissociative recombination, with an effective state representing the highest ($n \geq 6$) members of the series.

required now. The MQDT analysis of non-adiabatic perturbations in the low-lying Rydberg states of H_3 (Stephens & Greene 1995) is a promising way to tackle this problem.

(b) *Long-range dynamics and branching ratios*

Besides the rates for dissociative recombination, it is crucial for the study of equilibrium in atmospheric or interstellar media to know the outcome of a given recombination process, especially in the case of polyatomic ions. Recent experiments (Zajfmann *et al.* 1995; Datz *et al.* 1995; van der Zande *et al.* 1997; Semaniak *et al.* 1997) are very promising. They yield not only the energy distribution of fragments but also their angular distribution, related to the symmetry of the dissociative states involved. Theoretical support is clearly needed to help the analysis, but very little has been done for the calculation of branching ratios up to now. This aspect involves a 'half collision' between heavy particles, atomic or molecular partners, and requires quite different theoretical tools (e.g. close-coupling methods) than for the short range calculation of total cross sections. The dissociative molecular states often undergo severe configuration mixing on their way to dissociation, as well as non-adiabatic couplings, and their evaluation is the major bottleneck to accurate calculations of branching ratios. The long-range dynamics have been well studied in simple cases like $\text{H} + \text{H}$, $\text{H}^+ + \text{H}^-$ collisions (see, for example, Sidis *et al.* 1983) at high energy. This type of study provides enough data to 'graft' a close-coupling atomic collision calculation to the MQDT treatment of the first steps of DR, as was done already for the inverse process of associative ionization (Urbain 1990; Urbain *et al.* 1991).

Extensions to other molecules can be planned at least for qualitative results, and this aspect of DR studies is certainly worth theoretical efforts in the coming years.

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References

- Amitay, Z., Zajfman, D., Forck, P., Heupel, T., Grieser, M., Habs, D., Repnow, R., Schwalm, D. & Wolf, A. 1996a *Phys. Rev. A* **53**, R644.
- Amitay, Z., Zajfman, D., Forck, P., Hechtfisher, U., Seidel, B., Grieser, M., Habs, D., Repnow, R., Schwalm, D. & Wolf, A. 1996b *Phys. Rev. A* **54**, 4032.
- Bardsley, J. N. 1968 *J. Phys. B* **1**, 365.
- Carata, L., Schneider, I. F. & Suzor-Weiner, A. 1997. (In preparation.)
- Collins, L. A., Schneider, B. I. & Noble, C. J. 1992 *Phys. Rev. A* **45**, 4610.
- Collins, L. A., Schneider, B. I. & Noble, C. J. 1995 *Phys. Rev. A* **52**, 3010.
- Datz, S., Sundström, G., Biederman, Ch., Broström, S., Danared, H., Mannervik, S., Mowat, J. R. & Larsson, M. 1995 *Phys. Rev. Lett.* **74**, 896.
- Dehmer, P. M., Miller, J. M. & Chupka, W. A. 1984 *J. Chem. Phys.* **80**, 1030.
- Forck, P. 1994 Ph.D. thesis, Universität Heidelberg.
- Forck, P., Grieser, M., Habs, D., Lampert, A., Repnow, R., Schwalm, D., Wolf, A. & Zajfman, D. 1993a *Phys. Rev. Lett.* **70**, 426.
- Forck, P., Grieser, M., Habs, D., Lampert, A., Repnow, R., Schwalm, D., Wolf, A. & Zajfman, D. 1993b *Nucl. Instrum. Methods Phys. Rev. B* **79**, 273.
- Forck, P., Broude, C., Grieser, M., Habs, D., Kenntner, J., Liebmann, J., Repnow, R., Schwalm, D., Wolf, A., Amitay, Z. & Zajfman, D. 1994 *Phys. Rev. Lett.* **72**, 2002.
- Geddes, J., Dunn, K. F., Kouchi, N., McDonald, M. A., Srigengan, V. & Latimer, C. J. 1994 *J. Phys. B* **27**, 2961.
- Giusti, A. 1980 *J. Phys. B* **13**, 3867.
- Giusti-Suzor, A. 1989 In *Dissociative recombination: theory, experiments and applications* (ed. J. B. Mitchell & S. L. Guberman), p. 14. Singapore: World Scientific.
- Giusti-Suzor, A. & Lefebvre-Brion, H. 1980 *Chem. Phys. Lett.* **76**, 132.
- Giusti-Suzor, A. & Lefebvre-Brion, H. 1984 *Phys. Rev. A* **30**, 3057.
- Giusti-Suzor, A., Bardsley, J. N. & Derkits, C. 1983 *Phys. Rev. A* **28**, 682.
- Giusti-Suzor, A., Schneider, I. F. & Dulieu, O. 1993 In *Dissociative recombination: theory, experiments and applications* (ed. B. E. Rowe, J. B. Mitchell & A. Canosa), p. 11. NATO ASI series B313.
- Guberman, S. L. 1983 *J. Chem. Phys.* **78**, 1404.
- Guberman, S. L. 1991 *Geophys. Res. Lett.* **18**, 1051.
- Guberman, S. L. 1993 In *Dissociative recombination: theory, experiments and applications* (ed. B. E. Rowe, J. B. Mitchell & A. Canosa), p. 47. NATO ASI series B313.
- Guberman, S. L. 1994 *Phys. Rev. A* **49**, R4277.
- Guberman, S. L. & Giusti-Suzor, A. 1991 *J. Chem. Phys.* **95**, 2602.
- Jungen, Ch. & Dill, D. 1980 *J. Chem. Phys.* **73**, 3338.
- Kanfer, S. & Shapiro, M. 1983 *Laser Chem.* **3**, 73.
- Kilgus, G. *et al.* 1992 *Phys. Rev. A* **46**, 5730.

- Larsson, M. 1995 *Int. J. Mass Spectr. Ion Proc.* **149/150**, 403.
- Larsson, M., Danared, H., Mowat, J. R., Sigray, P., Sundström, G., Bsoström, L., Fiterich, A., Källberg, A., Mannervik, S., Rensfelt, K. G. & Datz, S. 1993 *Phys. Rev. Lett.* **70**, 430.
- Latimer, C. J., Dunn, K. F., O'Neill, F. P. O., MacDonald, M. A. & Kouchi, N. 1995 *J. Chem. Phys.* **102**, 722.
- Mitchell, J. B. A. 1990 *Phys. Rep.* **186**, 215.
- Mul, P. M., Mitchell, J. B. A., D'Angelo, V. S., Defrance, P., McGowan, J. Wm. & Froelich, H. R. 1981 *J. Phys. B* **14**, 1353.
- Nakashima, K., Takagi, H. & Nakamura, H. 1987 *J. Chem. Phys.* **86**, 726.
- Orel, A. & Kulander, K. C. 1993 *Phys. Rev. Lett.* **71**, 4315.
- Orel, A., Rescigno, T. N. & Lengsfeld, III, B. H. 1991 *Phys. Rev. A* **44**, 4328.
- Orel, A., Kulander, K. C. & Rescigno, T. N. 1995 *Phys. Rev. Lett.* **74**, 4807.
- Sarpal, B. K., Tennyson, J. & Morgan, L. A. 1994 *J. Phys. B* **27**, 5943.
- Sato, H. & Hara, S. 1986 *J. Phys. B* **19**, 2611.
- Schmidt, H. T., Vejby-Christensen, L., Pedersen, H. B., Kella, D., Bjerre, N. & Andersen, L. H. 1996 *J. Phys. B* **29**, 5943.
- Schneider, I. F., Dulieu, O. & Giusti-Suzor, A. 1991 *J. Phys. B* **24**, L289.
- Schneider, I. F., Dulieu, O., Giusti-Suzor, A. & Roueff, E. 1994 *Ap. J.* **424**, 983.
- Schneider, I. F., Strömholm, C., Carata, L., Urbain, X., Larsson, M. & Suzor-Weiner, A. 1997 *J. Phys. B* **30**, 2687.
- Semaniak, J., Rosen, S., Sundström, G., Strömholm, C., Datz, S., Danared, H., af Ugglas, M., Larsson, M., Van der Zande, W. J., Amitay, Z., Hechtfisher, U., Grieser, M., Repnow, R., Schmidt, M., Schwalm, D., Wester, R., Wolf, A. & Zajfman, D. 1996 *Phys. Rev. A* **54**, R4617.
- Shimamura, I., Noble, C. J. & Burke, P. G. 1990 *Phys. Rev. A* **45**, 4610.
- Sidis, V., Fussen, D. & Kubach, C. 1983 *Phys. Rev. A* **27**, 2431.
- Stephens, J. A. & Greene, C. H. 1995 *J. Chem. Phys.* **102**, 1579.
- Strömholm, C., Schneider, I. F., Sundström, G., Carata, L., Danared, H., Datz, S., Dulieu, O., Källberg, A., af Ugglas, M., Urbain, X., Zengin, V., Suzor-Weiner, A. & Larsson, M. 1995 *Phys. Rev. A* **52**, R4320–4323.
- Sundström, G., Datz, S., Mowat, J. R., Danared, H., Carlson, M., Broström, S., Mannervik, S. & Larsson, M. 1994 *Phys. Rev. A* **50**, R2806.
- Takagi, H. 1993 *J. Phys. B* **26**, 4815.
- Takagi, H. 1996 *Proc. 1995 Workshop on 'Dissociative Recombination: Theory, Experiment and Applications III'* (ed. D. Zajfman, J. B. A. Mitchell, D. Schwalm & B. R. Rowe), pp. 174–183. Singapore: World Scientific.
- Takagi, H., Kosugi, N. & Le Dourneuf, M. 1991 *J. Phys. B* **24**, 711.
- Tanabe, T., Katayama, I., Inoue, N., Chida, K., Arakaki, Y., Watanabe, T., Yoshizawa, M., Ohtani, S. & Noda, K. 1993 *Phys. Rev. Lett.* **70**, 422.
- Tanabe, T., Katayama, I., Kamegaya, H., Chida, K., Arakaki, Y., Watanabe, T., Yoshizawa, M., Saito, M., Haruyama, Y., Hosono, K., Hatanaka, K., Honma, T., Noda, K., Ohtani, S. & Takagi, H. 1995 *Phys. Rev. Lett.* **75**, 1066.
- Tennyson, J. 1996 *Atomic Data and Nuclear Data Tables* **64**, 253.
- Tennyson, J. & Noble, C. J. 1985 *J. Phys. B* **18**, 155.
- Urbain, X. 1990 Ph.D. thesis, Université de Louvain-la Neuve, Belgium.
- Urbain, X., Cornet, A., Brouillard, F. & Giusti-Suzor, A. 1991 *Phys. Rev. Lett.* **66**, 1685.
- Van der Donk, P., Yousif, F. B., Mitchell, J. B. A. & Hickman, A. P. 1991 *Phys. Rev. Lett.* **67**, 42.
- Van der Zande, W. J., Semaniak, J., Zengin, V., Sundström, G., Rosén, S., Strömholm, C., Datz, S., Danared, H. & Larsson, M. 1996 *Phys. Rev. A* **54**, 5010.
- Weiner, J., Masnou-Seeuws, F. & Giusti-Suzor, A. 1989 *Adv. At. Mol. Opt. Phys.* **26**, 209.
- Zajfman, D., Amitay, Z., Broude, C., Forck, P., Seidel, B., Grieser, M., Habs, D., Schwalm, D. & Wolf, A. 1995 *Phys. Rev. Lett.* **75**, 814.

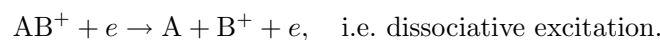
Discussion

J. TENNYSON (*Department of Physics and Astronomy, University College London, UK*). Latimer, Geddes and co-workers (Latimer *et al.* 1993; Geddes *et al.* 1995) interpret the results of their dissociative photoionization experiments on hydrogen to give resonance widths which strongly disagree with the theoretical ones Dr Suzor-Weiner uses for his dissociative recombination studies. Is it possible to use his MQDT methods to give a proper theoretical treatment of these experiments?

A. SUZOR-WEINER. Latimer *et al.* (1993) used a crude semi-classical approximation to extract the resonance width from their isotopic measurements of the *dissociative photoionization* cross sections



As outlined by Kirby (1995), this approximation implies an exponential decay of the resonance state which is not observed, and it then leads to an overestimated resonance width to compensate the too fast decay. A correct treatment of this process must be fully quantal and similar to the treatment of the related process



This process, competitive of dissociative recombination, is already included in our MQDT calculations at high energy, and the same approach could be applied to dissociative photoionization. However, MQDT is specially suited to handle series of bound Rydberg states which are generally no more present in this energy range, and more direct methods using a complex potential, in time-independent or time-dependent (Orel & Kulander 1996) formulations, are probably more efficient.

C. A. DE LANGE (*Laboratory for Physical Chemistry, Amsterdam University, The Netherlands*). We are currently performing relevant experiments with H_2 , and are in the process of measuring excitation to doubly excited Rydberg states converging upon dissociative ionic limits. We measure branching ratios into the various ($n = 2, 3, \dots$) excited H atoms.

Additional references

- Geddes, J., Dunn, K. F., Kouchi, N., McDonald, M. A., Srigengen, V. & Latimer, C. J. 1995 *J. Phys. B* **27**, 2961.
 Kanfer, S. & Shapiro, M. 1983 *J. Phys. B* **16**, L655.
 Kirby, K. P. 1996 *Symposium in honour of C. Bottcher, AIP Conf. Proc.* **347**, p. 43.
 Kirby, K. P., Uzer, T., Allison, A. C. & Dalgarno, A. 1981 *J. Chem. Phys.* **75**, 2820.
 Latimer, C. J., Dunn, K. F., Kouchi, N., McDonald, M. A., Srigengen, V. & Geddes, J. 1993 *J. Phys. B* **26**, L595.
 Latimer, C. J., Geddes, J., McDonald, M. A., Kouchi, N. & Dunn, K. F. 1997 *J. Phys. B* **29**, 6113.
 Orel, A. & Kulander, K. C. 1996 *Phys. Rev. A* **54**, 4992.

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