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Mats Larsson and Ann E. Orel
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1

Introduction

This book is focused on a single molecular process, dissociative recombination, and it may at first seem surprising that this topic can fill a whole book. As we shall see, it is not surprising when the complexity and applicability of the process are taken into account, and when the formidable challenges the process has provided to both experimenters and theorists are considered. This book brings together all the information we have on dissociative recombination in a single source, something which so far has been missing from the scientific literature.

A free electron which has a positive kinetic energy recombines with a positive atomic or molecular ion if its energy can be removed, so that it can enter a bound state. In the absence of a third body that can absorb the excess energy, the energy can be carried away by a photon. This is the only option for an atomic ion, and the process is inefficient. A molecular ion can make use of its internal structure and transfer the electron to a bound state while breaking one or several chemical bonds. This is a very efficient process that has taken its name from the fact that the capture of the electron is stabilized by dissociation. It is a primary chemical process, but is rarely described in chemical textbooks. It is the most complex of gas-phase reactions leading to the production of neutral atoms and molecules.

1.1 History 1900–1950

The process by which molecular ions recombine with electrons was for a long time strongly linked to discussions about the Earth's ionosphere. As we shall see later, it was not until after World War II that the research area initiated by the classic first recombination experiment of Thomson and Rutherford (1896) began to make contributions to the understanding of dissociative recombination. Initially, this research area was named "electrical discharges in gases"; it gradually transformed into gaseous electronics and plasma physics (see e.g. Loeb (1939) for the research in "gas discharge" physics before World War II).

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The possibility of a conducting layer in the Earth's atmosphere was first put forward in 1902 by Lodge (1902). He realized that solar radiation causes ionization, and that the presence of free electrons converts the atmosphere into a feeble conductor. His short note in *Nature* was inspired by an attempt by Joly (1902) to explain by invoking the aether how in December 1901 Marconi was able send radio waves (or wireless telegraphy, as it was also called) from Cornwall in England to St John's in Newfoundland (Canada) around the curved Earth (see Marconi (1910)). Lodge starts his note by saying that "I can assure Prof. Joly that his explanation will not do" (Lodge 1902, p. 222). The contribution by Lodge is less well known than the two independent suggestions of a conducting layer by Kennelly (1902) and by Heaviside (1902). The conducting layer soon became known as the Heaviside layer, the Kennelly–Heaviside layer, or the Heaviside–Kennelly layer. In the 1920s, Appleton and Barnett (1925a,b) provided the first experimental evidence of the Heaviside layer, and they also discovered a second layer at a higher altitude. Appleton was awarded the Nobel prize for physics in 1947 for this achievement. The second layer was for some time known as the Appleton layer, and in the citation for the Nobel prize it was stated that it was awarded "for his investigations of the upper atmosphere, especially for the discovery of the so-called Appleton layer." In the late 1920s the ionized layers began to be called the ionosphere, and Appleton used the labels E and F for the Heaviside and Appleton layers, respectively. Curiously, whereas Appleton named his Nobel lecture "The ionosphere" (Appleton 1949), this term was not used in the presentation of his Nobel prize by Hulthén (1949), a member of the Nobel Committee; instead "the Heaviside layer" and "the Appleton layer" were used. Using modern terminology, the ionosphere is a weakly ionized plasma embedded in the thermosphere, the hot, tenuous region above 80 km. The D region is about 75–95 km above the ground, the E region is 95−150 km above the ground, and the F1 and F2 layers are 150−200 km and 250−360 km above the ground, respectively.

The auroral green line at 5577 Å was first studied by Ångström (1869), but it was many decades before it was established that the origin of the green line is atomic oxygen (McLennan & Shrum 1925). Kaplan (1931) proposed that the auroral green line arises if ionized molecular oxygen recombines with electrons, so that atomic oxygen in the ^{1}S state is formed. A transition from the ^{1}S state to a lower state would then give rise to radiation at 5577 Å; this is the first mention of dissociative recombination. It is known today that dissociative recombination is not the dominant source of the O (^{1}S $\rightarrow$ ^{1}D) emission at 5577 Å in the aurora; energy transfer from excited molecular nitrogen to atomic oxygen is the currently favored principal source (Rees 1984). Nevertheless, as suggested by Kaplan dissociative recombination is involved in the faint glow from the Earth's atmosphere known as the airglow. At 200 km, dissociative recombination of O_2^+ gives rise to the

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O(^{1}S $\rightarrow$ ^{1}D) transition at $\lambda = 5577$ Å. Because of its weakness, the study of the airglow spectrum was conducted much later than the auroral spectral studies. The auroral green line and the green airglow arise from the same transition in atomic oxygen, even if the precursors are different.

During the 1930s, much progress was made in understanding the ionosphere. Appleton (1949) developed techniques for exploring the ionosphere by means of reflection of radio waves, and these techniques were also adopted by other researchers. It was realized that electrons are primarily created by ionization by solar radiation in the ultraviolet, and that the ionization reaches a maximum about noon, falls off as sunset approaches, and continues to decrease during the night. Appleton (1937) summarized the knowledge of the ionosphere as of 1937 in his Bakerian lecture.

But if the source of electrons is photoionization, what could the sink of electrons be? And what process could account for the removal of electrons with a rate coefficient of the order of 10^{-8} cm^3 s^{-1}? Attachment of electrons to neutral atoms and molecules was put forward as one possibility, but in the long run this was difficult to reconcile with the results from the radio wave reflection measurements. Appleton (1937) favored recombination between electrons and positive ions, but did not try to sort out what the process could be at a detailed atomic and molecular level.

By the end of the 1930s atomic and molecular spectroscopy had a long history of making important contributions to space physics, but then atomic and molecular collision physics began to make an impact. Massey (1937) realized that a theoretical description of the upper atmosphere, with its resemblance to a gas in a low-pressure discharge source, necessarily would have to include individual collision processes that occur in such systems. The theory of layer formation was worked out by Chapman (1931), who showed that if ionizing radiation enters the atmosphere from above, the decrease in density of atmospheric constituents as a function of height, and hence the decrease in ionization density, is balanced by the decreasing radiation density as a function of decreasing height, and leads to the formation of a layer with a sharp ionization density maximum. Massey (1937) identified processes that could lead to the removal of electrons, and dismissed dissociative recombination of O_2^+, which was the molecular ion explicitly considered, for two reasons: it would require electrons within a narrow energy range in order to allow O_2^+ to capture an electron into an unstable O_2 state far above the dissociation limit, and it would have to rely on the weak interaction between electronic and nuclear motion. Furthermore, radiative recombination could be dismissed as well, since recombination by emission of a photon proceeds with a rate coefficient of the order of 10^{-12} cm^3 s^{-1}. This lack of a suitable electron–ion recombination process did not pose any problems to Massey at the time, since his conclusion of a 100:1 ratio, λ, between negative ions and electrons was in agreement with Chapman's theory of the variation of the Earth's magnetic field (Chapman 1931). It was also the prevailing view in the community working with electrical discharge that electron–ion recombination was an improbable process, and that the so-called volume recombination between ions (positive and negative) was the normal neutralizing process (Loeb 1939). Furthermore, the pioneering experiment by Kenty (1928), the first to provide a measurement of a rate coefficient that could be unambiguously ascribed to electron–ion recombination, had given 2×10^{-10} cm^3 s^{-1} as an upper limit to the recombination rate coefficient of Ar$^+$. Thus, Massey (1937) concluded that electrons are removed in the ionosphere by attachment followed by recombination of negative and positive ions.

New observational data by Appleton and Weekes (1939) made it difficult to uphold the view of a large excess of negative ions with respect to electrons in the ionosphere, and Massey's "back-of-the-envelope" estimates of the cross section for electron attachment to atomic oxygen did not survive more detailed quantum mechanical calculations (Bates & Massey 1943a). In the expression for an apparent recombination coefficient for electrons, $\alpha = \alpha_e + \lambda\alpha_i$, where α_e is the electron–ion recombination coefficient and α_i is that of mutual neutralization of positive and negative ions, the maximum value of λ was estimated to be 0.5 (Bates & Massey 1943b). This was possible to reconcile with the negative ion theory since the decrease in λ from 100 to 0.5 was compensated by an increase of α_i (Bates & Massey 1943a) as compared with Massey's (1937) original estimate. After a more careful analysis, however, λ was found to be only about 10^{-3} (Bates & Massey 1946), a value too small to be compensated by an increase of α_i. Forced to dismiss electron attachment to neutral atoms and molecules as a process for electron removal in the ionosphere, Bates and Massey (1946, p. 285) stressed that "[While] there are, as has been insisted, grave difficulties in the present theory of the ionized layers . . ." They did not consider dissociative recombination as being a fast process, but acknowledged that many difficulties would disappear if it were. In their second paper on this subject (Bates & Massey 1947), they discussed the process

$$O_2^+ + e^- \rightarrow O' + O'' \tag{1.1}$$

(O' and O'', using the notation in the original paper, refer to unspecified electronic states of the oxygen atom products) and concluded that it may, after all, proceed rapidly. The arguments, however, were indirect, and they admitted that there was not enough evidence to reach a firm conclusion.

The discussions about dissociative recombination had hitherto been driven entirely by problems related to the upper atmosphere (Kaplan 1931, Massey 1937, Bates & Massey 1943b, 1946, 1947). The breakthrough in establishing that

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dissociative recombination is a rapid process, however, came as a result of laboratory work at MIT that benefited from microwave equipment donated to MIT by the US army as thanks for the MIT contribution to the US war effort. Biondi and Brown (1949a) applied microwave techniques in order to study simultaneous (ambipolar) diffusion of electrons and positive ions in a pure helium afterglow plasma, making use of the superior accuracy of this new technique in measuring the electron density without perturbing the plasma. The analysis of the diffusion coefficient was complicated by the presence of electron−positive ion recombination, and they found that their data were best fitted if the recombination coefficient was 1.7×10^{-8} cm^3 s^{-1}. Bates (1950a) pointed out that such a large rate coefficient would most likely derive from He_2^+, which may be formed in the discharge.

Six months after their article on ambipolar diffusion, Biondi and Brown (1949b) published an article in which they reported recombination rate coefficients for a number of monatomic and diatomic gases. They found rate coefficients in the 10^{-8}–10^{-6} cm^3 s^{-1} range, and concluded that these coefficients were much larger than those predicted by the theory of radiative recombination. Microwave experiments at nearby Harvard University, which also included optical detection of the afterglow, gave similar results (Holt *et al*. 1950, Johnson, McClure, & Holt 1950). The results from these new experiments inspired Bates (1950b) to write his seminal article in which he explained how dissociative recombination of molecular ions with electrons can be very fast.

It is interesting to note that Bates's (1950a) explanation that He_2^+ could give a rate coefficient of the order of 10^{-8} cm^3 s^{-1} is incorrect, but was based on an experiment (Biondi & Brown 1949a) which is now known also to be incorrect! In fact, He_2^+ is one of the few molecular ions which recombines very slowly (Carata, Orel, & Suzor-Weiner 1999), and the rate coefficient given by Biondi and Brown (1949a) was not properly corrected for diffusion loss.

1.2 History 1950–1970

Bates (1950b) avoided the problem of the weak coupling between electronic and nuclear motions by invoking a two-step mechanism in which the electron first is captured by the molecular ion so that an unstable neutral molecule is formed, followed by rapid dissociation of the neutral molecule into its atomic constituents. The incoming electron interacts not with the heavy nuclei but with the electron cloud, and the fast dissociation prevents the electron from being transferred back to the continuum by autoionization. Bates derived an approximate formula for the rate coefficient, and by means of order of magnitude estimates, he arrived at a tentative rate coefficient of 10^{-7} cm^3 s^{-1}. But he also acknowledged the tremendous

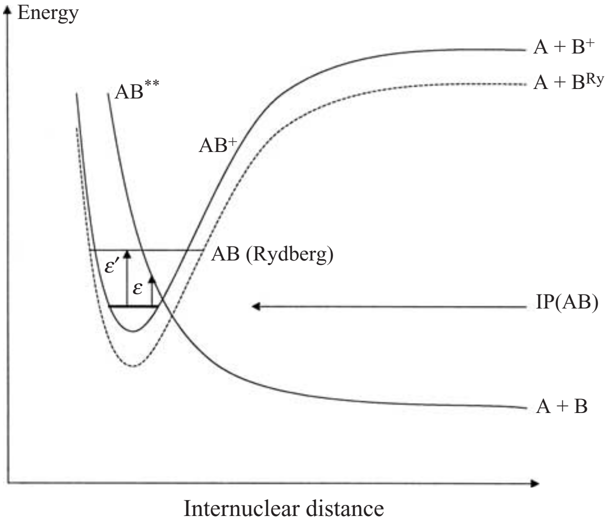

Figure 1.1 The dissociative recombination mechanism as proposed by Bates (1950b). The molecular ion AB$^+$ populating its lowest vibrational level collides with an electron with kinetic energy ε. The electron's kinetic energy is converted to electronic excitation energy, and the electron is captured by the ion so that a doubly excited neutral molecule AB** is formed. The molecule is unstable with respect to autoionization as long as the total energy of AB** is larger than the ionization energy, but because of the rapid movement of atoms A and B along the strongly repulsive curve, autoionization becomes prohibited, and the electron capture is stabilized. The cross section, σ, is proportional to $1/\varepsilon$.

difficulties of an accurate computation, and for the rest of the 1950s the development of the field of dissociative recombination was driven almost entirely by experiments (Bates & Dalgarno 1962).

Figure 1.1 shows a schematic representation of the potential energy curves involved in the dissociative recombination process. It follows from the figure that atoms A and B will receive kinetic energy in excess of thermal energy. If either A or B is produced in an excited state, spectral line broadening would result. Thus, it was early realized that optical observations of the afterglow would be one way of establishing the mechanism proposed by Bates (1950b). The other obvious route was to ascertain that the afterglow contained molecular ions, something which required the addition of a mass spectrometer to the afterglow apparatus. In practice, these experimental additions to the afterglow technique took some time before being fully implemented and giving conclusive results. A helium afterglow was used to search for broadening of the $\lambda = 5876$ Å ($3\,^3D \rightarrow 2\,^3P$) line, but because of the very slow recombination of He_2^+ with thermal electrons (unknown at the time), the results were inconclusive (Biondi 1956). Although a mass spectrometer was added to an afterglow apparatus at an early stage

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More information

(Phelps & Brown 1952), most afterglow studies were performed without mass identification.

In the 1960s, Connor and Biondi (1965) and Frommhold and Biondi (1969) carried out a series of afterglow studies of Ne_2^+ that finally established that emission lines from the afterglow are composed of a broad part arising from dissociating, energetic Ne atoms, and a narrower part arising from thermal Ne atoms that have transferred most of their kinetic energy to residual atoms before radiating.

An important addition to Bates's (1950b) mechanism was made in 1968 by Bardsley (1968b), although the idea had already been outlined in the abstract book from the *Fifth International Conference on the Physics of Electronic and Atomic Collisions* in Leningrad, USSR, in 1967 independently by Bardsley (1967) and Chen and Mittleman (1967). They proposed that the electron can also surrender its kinetic energy by exciting a vibrational mode in the molecule while being captured into a Rydberg state which is member of a Rydberg series that converges to the ion core. In a second step, the Rydberg state is predissociated by an electronically doubly-excited, repulsive state. Bardsley (1967, 1968a,b) labeled this mechanism as the indirect one, to distinguish it from the direct mechanism of Bates (1950b). It is interesting to note how Chen and Mittleman (1967) assessed the complexity of the process: "Thus we are faced with an extremely complex problem the results of which depend critically upon the details of molecular states which are prohibitively difficult to obtain for even the simplest molecule."

By the end of the 1960s, only the rare gas dimers, the most important atmospheric ions, such as N_2^+, O_2^+, and NO^+, and a few other systems had been investigated experimentally. No *ab initio* calculations had been performed. Two comprehensive reviews had been published (Danilov & Ivanov-Kholodny 1965, Bardsley & Biondi 1970), along with a shorter review by Biondi (1964), and a theoretical review of significant importance to dissociative recombination (O'Malley 1971).

1.3 History 1970–1990

One ion is conspicuously missing from the list given at the end of the previous section – H_2^+. In its capacity as the simplest molecule structure, it is ideal for a comparison of experiment and theory. The problem of studying dissociative recombination of H_2^+ in a decaying plasma is that it is very rapidly converted to H_3^+ by the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$. Thus, the techniques developed up to 1970, which were all based on the reaction rate coefficient being obtained by measuring the decay in concentration of charged particles when an ionizing agent was removed, were unsuitable for the study of H_2^+. In the early and mid 1970s, several new techniques were developed which aimed at measurement of cross section rather than rate coefficient.

Peart and Dolder (1971) developed a technique in which a beam of electrons crossed a beam of ions at a 10° angle, and used it to measure the cross section for dissociative recombination of D_2^+ (Peart & Dolder 1973a) and H_2^+ (Peart & Dolder 1974a). Dunn and coworkers (Phaneuf, Crandall, & Dunn 1975, Vogler & Dunn 1975) used crossed beams to study the atomic products following dissociative recombination of D_2^+. Finally, McGowan, Caudona, and Keyser (1976) developed a merged-beam technique, which they used to study the dissociative recombination of a range of molecular ions, including H_2^+.

Walls and Dunn (1974) combined a static ion trap with an electron beam to measure the cross section for dissociative recombination of O_2^+ and NO^+. This is the first application of a technique which makes use of stored ions. Mathur, Kahn, and Hasted developed a different type of trap technique (1978).

There was also a development of afterglow techniques. A shock-tube technique was developed by Fox and Hobson (1966) and Cunningham and Hobson (1969, 1972a), and allowed studies of recombination at elevated electron *and* ion temperatures. In the context of elevated temperatures, the studies of recombination in flames should also be mentioned (see e.g. Butler and Hayhurst (1996)). Sauer and Mulac (1971, 1972, 1974) performed a few recombination rate coefficient measurements by observing the time-dependent emission from recombination end products using the pulse radiolysis technique. (In pulse radiolysis, an important technique in radiation chemistry, the ionizing source is pulses of electrons, usually from Van de Graaf accelerators of energy 2–4 MeV; a single-volume description is given by Matheson and Dorfman (1969).) Building on the flowing afterglow technique developed by Ferguson and coworkers (Fehsenfeld *et al*. 1965, Goldan *et al*. 1965) to study ion–neutral reactions, Smith and Adams (1983) developed the technique to also allow studies of positive ion–negative ion reactions. In a flowing afterglow, a flow tube with a large Roots-type pump is used to force a carrier gas to flow towards the pump. Ionization occurs upstream of the flow by chemi-ionization (ion–neutral reactions) or some other type of ionization. In order to study positive ion–negative ion reactions, Smith and Adams supplied their flow tube with a Langmuir probe, which allowed the measurement of the charge density as a function of position along the tube. With some modification, the flowing afterglow/Langmuir probe (FALP) technique could be used to measure dissociative recombination rate coefficients (Alge, Adams, & Smith 1983). It is less well known that Mahdavi, Hasted, and Nakshbandi (1971) performed a flowing afterglow study of recombination more than a decade before the FALP technique appeared. Apparently only one experiment was performed by Hasted's group.

During the period leading up to 1970, the focus had been on measuring rate coefficients and establishing the mechanism. The afterglow techniques now started also to address the question of product state distributions. To begin with the atomic

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Excerpt
More information

states into which a diatomic ion recombines were identified (Zipf 1970). Later, the breakup of polyatomic molecular ions in dissociative recombination was studied by optical techniques (Vallée *et al*. 1986), as reviewed in detail by Adams (1992). The beam techniques also addressed these problems for diatomic (Phaneuf, Crandall, & Dunn 1975, Vogler & Dunn 1975) and polyatomic (Mitchell *et al*. 1983) systems, but in contrast to the afterglow techniques, these were the only efforts with beam techniques until the advent of the ion storage rings.

Holt *et al*. (1950) had used optical methods to monitor the decaying plasma in an afterglow. A modern version of this method was employed by Amano (1988, 1990), who used an infrared laser to monitor the ion concentration in an afterglow. With a narrow band laser, Amano could for the first time measure the disappearance of ions in specific quantum states.

The rapid experimental development of the field of recombination during the 1970s and 1980s is well described in a number of review articles (Biondi 1973, Dolder & Peart 1976, 1986, Berry & Leach 1979, Eletskii & Smirnov 1982, Mitchell & McGowan 1983, Compton & Bardsley 1984, McGowan & Mitchell 1984, Mitchell 1986, 1990a,b, Johnsen 1987, Adams & Smith 1988a,b).

There was also an impressive development of theoretical methods during this period, partly inspired by the data for the simplest molecular ion. Nielsen and Berry (1971) performed the first *ab initio* calculations on H_2^+, but included only the direct mechanism. Bottcher developed a projection operator formalism (Bottcher 1974) and applied it to H_2^+ (Bottcher 1976). Although both the direct and indirect mechanisms were included, they were treated separately. Lee (1977) and Giusti (1980) showed how multichannel quantum-defect theory (MQDT) can be used to treat dissociative recombination, including a unified treatment of the direct and indirect processes. Giusti-Suzor, Bardsley, and Derkits (1983) showed that configuration interaction theory and MQDT are two alternative ways of treating dissociative recombination, and applied both methods to H_2^+, thus making possible a comparison of experiment (Auerbach *et al*. 1977) and theory. Although a strict comparison was impaired by the undetermined H_2^+ vibrational distribution in the experiment, theory was nevertheless able to support the existence of the narrow window resonances observed in the experiment, and could show how they arise from interferences between direct and indirect dissociative recombination. Such resonances also emerged from O'Malley's (1981) treatment of the direct mechanism, in which he allowed for the Rydberg states involved in the indirect process to play a role. A more detailed comparison would take several more years to realize, including efforts to produce H_2^+ primarily in its lowest vibrational level, however, the essential physics is captured in the papers of Giusti (1980) and Giusti-Suzor, Bardsley, and Derkits (1983). This work provided the framework for understanding dissociative recombination. The theoretical development has been reviewed by Giusti-Suzor (1986) and Guberman (1986).

Although H_2^+ is the ideal system for comparison of experiment and theory, other molecular systems occupied more important roles in atmospheric physics and astrophysics. The need for a consistent approach to the construction of potential curves of relevance to dissociative recombination was quickly realized (Guberman 1983a).

1.4 History 1990–present

The development of heavy-ion storage rings for atomic and molecular physics (see e.g. Larsson (1995a) for a review) led to a boost of the study of dissociative recombination. This development will not be described here, but rather in the subsequent chapters of this book. The first papers on the subject based on work using ion storage rings were published in a single issue of *Physical Review Letters* (Tanabe *et al*. 1993, Forck *et al*. 1993b, Larsson *et al*. 1993a). The development of the techniques established prior to 1990 will also be described.

The crossing of potential curves, as shown in Fig. 1.1, exercised a strong influence on the scientific community involved in dissociative recombination research (too strong, Bates (1994) would argue). In the early 1990s, an increasing amount of experimental data made it difficult to uphold the view that a crossing of the ion potential curve by a neutral state potential curve is required to drive dissociative recombination. Estimates based on semiclassical treatment (Bates 1992b, 1993a) and *ab initio* calculations (Guberman 1994, Sarpal, Tennyson, & Morgan 1994) made it clear that dissociative recombination can be quite effective even in the absence of a curve crossing.

Conferences with dissociative recombination as the central theme have been organized from 1988 onwards in an ad hoc fashion, and the proceedings from these conferences give a very good coverage of the development of the field (Mitchell & Guberman 1989, Rowe, Mitchell, & Canosa 1993, Zajfman *et al*. 1996, Larsson, Mitchell, & Schneider 2000, Guberman 2001, 2003a, Wolf, Lammich, & Schmelcher 2005). Several review articles also describe the development (Adams 1992, 1993, Glosik 1992, Bates 1994, Flannery 1994, Mitchell 1995, Larsson 1995a,b, 1997, 2000a, 2001, Larsson & Thomas 2001, Johnsen & Mitchell 1998, Adams, Babcock, & McLain 2003, Guberman 2003b, Petrie & Bohme 2003, Florescu-Mitchell & Mitchell 2006, Adams, Poterya, & Babcock 2006). The review by Florescu-Mitchell and Mitchell (2006) contains a complete listing of experimental results until the end of 2005. A database which builds on the compilation by Florescu-Mitchell and Mitchell (2006) is available at URL: http://mol.physto.se/DRdatabase.