Electron Attachment and Recombination in Dense Molecular Media*

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Abstract
A survey is given of experimental studies of electron attachment and recombination in dense molecular media, from which information on the effect of van der Waals potentials or on the existence of surrounding molecules on these processes is obtained.

1. Introduction
The investigation of the dynamic behaviour of low-energy electrons such as electron transport and reactivities in dense molecular media is of essential importance in both fundamental and applied sciences (Hatano and Shimamori 1981; Warman 1982; Christophorou and Sionos 1984; Johnsen and Lee 1985; Morgan 1985; Hatano 1986, 1994; Freeman 1987; Holroyd 1987; Holroyd and Schmidt 1989; Shinsaka and Hatano 1990, 1993; Sanche 1991).

Values of the electron mobility $\mu_e$ have been measured extensively in a variety of dense molecular media and several theoretical models have been proposed for the transport mechanism. Electron reactivities with solute molecules or positive ions in these media have been also extensively investigated. The former reaction is electron attachment and the latter electron–ion recombination. The investigation of these electron reactivities has provided new insight into the behaviour of low-energy electrons in matter. In the following, a brief survey is given of the investigation of these electron reactivities, divided into attachment and recombination to summarise distinctive features of these reactivities in dense molecular media, as compared to those in low density gases as well as in beams.

2. Electron Attachment in Dense Gases
Electron attachment is a process in which electrons are captured by atoms or molecules to form negative ions and classified into two types; dissociative and

* Dedicated to Professor Robert W. Crompton on the occasion of his seventieth birthday.
non-dissociative processes as shown in the following reaction scheme (Hatano and Shimamori 1981; Christophorou et al. 1984; Hatano 1986):

\[ e^- + AX \xrightarrow{\sigma \text{ or } k \frac{1}{\tau}} AX^-* \xrightarrow{} A + X^- \quad (1) \]

\[ \xrightarrow{\text{1/}\tau} AX^- + \text{energy}. \quad (2) \]

Interaction of low-energy electrons with molecules, AX, produces unstable negative ions, AX$^-*$, with a cross section $\sigma$ or a rate constant $k$. The autodetachment of electrons from AX$^-*$ with a lifetime $\tau$ may compete with the dissociation of AX$^-*$ or with the formation of stable molecular negative ions, AX$^-$, which requires the release of excess energy from AX$^-*$. The lifetime $\tau$ is related to the electron-energy width of the attachment resonance. The value of $1/\tau$ is a rate constant for the autodetachment process. In the presence of third-body molecules or in bulk media, AX$^-*$ is collisionally stabilised to form stable AX$^-$. The branching ratios among the unimolecular processes of decaying AX$^-*$ depend on the interrelationship of the potential energy curves between AX and AX$^-$, and also on electron energies. The relative importance of the collisional stabilisation process in the overall decay processes of electrons depends largely on these unimolecular processes, particularly the lifetime $\tau$ and on the number density and character of third-body molecules, in which one may expect some environmental effects on the overall scheme of the electron attachment processes. In addition to the determination of cross sections or rate constants for electron attachment or negative-ion formation and their electron energy dependences, it has been of prime importance in electron attachment studies to clarify the attachment mechanism, not only the two-body mechanism but also the overall mechanism, and how environmental conditions affect the mechanism (Hatano and Shimamori 1981; Hatano 1986).

Electron attachment processes have been extensively studied theoretically and experimentally, and these have been comprehensively summarised in several review

Table 1. Experimental methods for electron attachment studies (Hatano 1986, 1991; Christophorou et al. 1984)

<table>
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<tr>
<th>(A) Beam methods</th>
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<tr>
<td>(1) Electron scattering spectroscopy</td>
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<td>(2) Electron impact mass spectroscopy of negative ions</td>
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<td>(3) Photo-electron spectroscopy of negative ions</td>
</tr>
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<td>(4) Collision of Rydberg atoms with molecules</td>
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<td>(5) Collision of alkali metal atoms with molecules</td>
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<tr>
<td>(6) Photoelectron attachment to molecules</td>
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</tbody>
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<table>
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<tr>
<th>(B) Swarm methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Electron swarm (or drift tube) techniques</td>
</tr>
<tr>
<td>(2) Microwave techniques combined with flowing or static afterglow methods (or with electrical discharges)</td>
</tr>
<tr>
<td>(3) Microwave techniques combined with pulse radiolysis methods</td>
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<td>(4) Electron cyclotron resonance spectroscopy</td>
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<td>(5) Pulse sampling technique</td>
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<tr>
<td>(6) Electron density sampling method (the Cavalleri method)</td>
</tr>
</tbody>
</table>
papers (Hatano and Shimamori 1981; Christophorou et al. 1984; Hatano 1986, 1994; Shimamori 1991; Chutjian 1992; Sanche 1994; Illenberger 1994; Bardsley 1994; Dunning 1995; Hotop et al. 1995). Experimentally, low-energy electron attachment to molecules has been studied using both beam and swarm methods. Each of them, as listed in Table 1, consists of several different techniques depending on the method of detecting low-energy electrons or the negative ions formed (Hatano 1986, 1991; Christophorou et al. 1984).

Various types of electron scattering experiment at energies less than several electron volts have given cross sections for electron attachment and information on the initial interaction potential between an electron and molecule, and thus provided knowledge on the structure of the negative ions formed. Generally, however, it has been very difficult to perform electron attachment experiments using beam methods at extremely low energies, particularly near thermal energies. Heavy particle collisions such as those using Rydberg atoms (Dunning 1995; Hotop et al. 1995) and alkali metal atoms (Lacman 1980) as low-energy electron sources have been a good substitute, giving important information on electron attachment processes. Recent progress in photoelectron attachment studies has been very informative in understanding the attachment mechanism at extremely low energies (Chutjian 1992; Hotop et al. 1995).

Instead of beam methods, electron swarm or drift tube techniques have played a major role in electron attachment studies at low energies and lead to data on attachment rate constants, their electron energy dependences, and the negative ions formed (Crompton 1979; Christophorou et al. 1984). Most electron swarm studies monitor the rate of removal of electrons in the swarm drifting in a tube, in most cases, under DC electric field in the presence of a buffer gas. Christophorou and co-workers (Christophorou 1976, 1978a, 1978b; Christophorou et al. 1984) have extensively studied electron attachment in dense gases as quasiliquids using their swarm technique. In addition to usual swarm techniques, an interesting approach of measuring cyclotron resonance signals due to free electrons in gases has been carried out for the study of electron attachment to various molecules as a function of electron energy (Mothes et al. 1972). Another interesting approach to electron attachment studies is highly sensitive monitoring of electron density in a swarm by the Cavalleri method (Cavalleri 1969; Hegerberg and Crompton 1983). The pulse sampling technique is simple but capable of yielding precise data, particularly on energies of negative-ion formation (Wentworth and Steelhammer 1968). A microwave technique for monitoring the rate of removal of electrons in a swarm was combined with static or flowing afterglows produced by electrical discharges (Biondi 1951, 1963). This technique has been combined also with the pulse radiolysis method (Hatano 1989, 1991), in order to eliminate inherent limitations in the abovementioned microwave technique (Hatano and Shimamori 1981; Hatano 1986; Shimamori and Hatano 1976; Shimamori 1991). The response time of the detection system for electrons has been greatly improved and the effect of the presence of various species in afterglows on electron attachment processes has been eliminated. This combination, therefore, has given reasonably good selectivity for measuring electron attachment processes even in multiple collision systems. For the study of the electron attachment mechanism, ordinary swarm techniques have several experimental limitations since only a few environmental buffer gases can be used for which the swarm parameters and electron energy
distributions are well known. Therefore, in cases where the attachment mechanism is strongly dependent on the particular nature of the environmental gas, the technique may not give enough information to evaluate adequately the mechanism in detail. On the other hand, the microwave technique has been used as an alternative means for such studies, with the main advantage of the technique being that it allows observation of the behaviour of thermal electrons, thus excluding any factor dependent on the electron energy distribution. In the investigation of low-energy electron attachment in bulk gases particularly in dense gases, therefore, a microwave cavity technique combined with a pulse-radiolysis method has shown a distinct advantage over the other techniques, because a sensitive detection of the time-resolved density of thermal and epithermal electrons is practicable with very fast response over a wide range of densities of the environmental gas, which can be chosen with virtually no limitations (Hatano and Shimamori 1981; Hatano 1986; Shimamori 1991). The technique therefore provides the absolute values of $k$ and $\tau$ and also quantitative information on the effect of the density of environmental third-body molecules on these values, i.e. the absolute values of third-body attachment rate constants. Thus, the mechanism of low-energy electron attachment to molecules has been discussed primarily in terms of the interaction of electrons with molecules even in a multiple collision system. Recently a new technique has been further developed in the pulse radiolysis microwave cavity method. This is the combination of microwave heating with their method, providing the ability to change the electron energy in the cavity from thermal to about 1 eV (Shimamori et al. 1992; Shimamori 1995).

The studies of thermal electron attachment to O$_2$, N$_2$O and other molecules using the pulse radiolysis microwave cavity method have revealed interesting features of electron attachment to van der Waals (vdW) molecules (Hatano and Shimamori 1981; Hatano 1986, 1994; Itikawa et al. 1989), i.e. the effect of the vdW potential on the electron attachment resonance. This experiment has been complemented by beam experiments on electron collisions with vdW molecules (Mark et al. 1985; Stamatovic 1988).

<table>
<thead>
<tr>
<th>(O$_2$.M)</th>
<th>$k$ ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)</th>
<th>$E_r$ (meV)</th>
<th>$\Gamma$ ($\mu$eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O$_2$.N$_2$)</td>
<td>3000</td>
<td>20</td>
<td>800</td>
</tr>
<tr>
<td>(O$_2$.C$_2$H$_6$)</td>
<td>1100</td>
<td>30</td>
<td>450</td>
</tr>
<tr>
<td>(O$_2$.C$_2$H$_4$)</td>
<td>380</td>
<td>45</td>
<td>270</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3</td>
<td>88</td>
<td>10</td>
</tr>
</tbody>
</table>

The rate constants for electron attachment to vdW molecules (e.g. O$_2$.M and N$_2$O.M where $M$ is O$_2$, N$_2$O or any other molecule) are much larger than those for electron attachment to isolated O$_2$ or N$_2$O. The results are summarised in Table 2 for O$_2$ and O$_2$.M, which clearly shows that electron attachment to an ordinary isolated single molecule is greatly enhanced by the presence of a surrounding guest molecule $M$. In Table 2 a good correlation is observed between an enhancement of $k$ due to $M$ and a decrease in the value of $E_r$ or an increase in the value of $\Gamma$. The value of $\Gamma$, 10 $\mu$eV, for the electron attachment to O$_2$
corresponds to a lifetime $\tau$ of $O_2^{-}(X^2\Pi_g, v' = 4) \rightarrow O_2 (X^3\Sigma^+_-) + e^-$ which is about 100 ps. The modification of the interaction potential between an electron and isolated single molecule by the formation of the vdW molecule, which is shown schematically in Fig. 1, reflects the departure from gas-phase characteristics toward those of the condensed phase. The effect of the vdW potential or of the presence of a surrounding molecule on electron attachment can be summarised as follows (Hatano 1986, 1994):

1. a lowering of the attachment resonance energy due to a deeper ion–neutral potential in comparison with the neutral–neutral potential of the vdW molecule (see Fig. 1);
2. additional vibrational structures of the vdW molecule;
3. a symmetry breaking due to the vdW interaction which allows the molecule to attach the electron with additional partial waves;
4. a deformation of the molecular structure or the change of the vibrational modes due to the surrounding molecules; and
5. an effective vibrational relaxation of the negative ion formed with excess energy due to the presence of a built-in third-body molecule in a vdW molecule.

The distinct features of electron attachment to vdW molecules as summarised above have been a substantial clue to understanding the fundamental nature of electron attachment, not only in dense gases but also in the condensed phase (Hatano and Shimamori 1981; Hatano 1986, 1994). It is also apparent that most electron attachment in bulk systems is no longer a simple process consisting of the interaction of an electron with an isolated molecule, but is affected by the presence of a surrounding molecule. From this point of view, interesting phenomena in ionised gases such as the attachment cooling effect (Crompton...
et al. 1980; Koura 1982, 1983; McMahon and Crompton 1983; Skulderud 1983) and the response time of the air-filled fast response ionisation chamber (Boag 1984; Fessenden 1985) should be analysed by taking into account the important role of vdW molecules in the electron attachment mechanism.

3. Electron–Ion Recombination in Dense Molecular Media

It is of great interest to investigate also electron–ion recombination in dense molecular media in the density range from dense gases to liquids and solids (Shinsaka and Hatano 1990, 1993; Hatano 1994) because the Coulombic interaction distance between an electron and ion as expressed by the Onsager length $r_c$ is much larger than the mean intermolecular distance of the nearest neighbour molecules in the medium:

$$r_c = \frac{e^2}{\epsilon k_B T},$$

where $e$, $k_B$, $\epsilon$ and $T$ are the electron charge, the Boltzmann constant, the dielectric constant of the medium, and the absolute temperature of the medium respectively.

Electron–ion recombination processes in isolated two-body collisions or in low pressure gases have been extensively studied mainly with a merged beam method (Mitchell and Yousif 1989), a pulsed afterglow method (Shiu et al. 1977), and a flowing afterglow method (Smith and Adams 1990). It should be noted that a new experimental method of recombination has been recently developed by means of a cooler ring (Tanabe et al. 1995; Muller 1995). In the gas phase at one to several atmospheric pressures, these processes have been studied with a pulse-radiolysis method (Warman et al. 1979; Sennhauser et al. 1980; Van Sonsbeek et al. 1992; Cooper et al. 1991), and the observed recombination rate constants $k_r$ are expressed by

$$k_r = k_2 + k_3 n,$$

where $k_2$ and $k_3$ are the two- and three-body coefficients respectively, and $n$ is the density of a third-body molecule. In dense media such as high pressure gases near the critical point, liquids, and solids, however, experimental and theoretical studies have been relatively very few, but recently they have made considerable progress (Shinsaka and Hatano 1990, 1993; Hatano 1994).

In the liquid phase, the observed electron–ion recombination rate constants $k_r$ in a variety of nonpolar media are, as shown in Fig. 2, in good agreement with the calculated values $k_D$ from the reduced Debye equation

$$k_D = \frac{4\pi e}{\epsilon \mu_e},$$

in the range of $\mu_e$ below about 150 cm$^2$ (V s)$^{-1}$. Thus, recombination in these media is taken to be diffusion controlled (Tezuka et al. 1983).
In liquid and high pressure gaseous methane in which most $\mu_e$ values are larger than 150 cm$^2$ (Vs)$^{-1}$, however, it has been found (Nakamura et al. 1983) that the observed $k_r$ values are much lower than $k_D$. This experiment has stimulated several theoretical investigations of the recombination process in dense media (Warman 1983; Morgan and Bardsley 1983; Tachiya 1986, 1987; Morgan 1986; Kaneko et al. 1988, 1990; Lopez-Quintela et al. 1988; Sceats 1989; Mozumder 1990, 1993, 1995; Lopez-Quintela and Bujan-Nunes 1991; Isoda et al. 1994). Since the electron mobilities in dense Ar, Kr, and Xe media are as high as in dense methane media, the values of $k_r$ and $\mu_e$ in these media have also been measured (Shinsaka et al. 1988, 1989; Honda et al. 1992, 1993; Ukai et al. 1995) and compared further with theoretical results. The observed $k_r$ values in these rare-gas media in both liquid and gas phases are again found to be much smaller than those calculated by the reduced Debye equation. In the solid phase, however, the observed $k_r$ values are almost in agreement with those calculated by equation (5). These results are summarised in Fig. 3. The effect of an external DC electric field strength on both $k_r$ and $\mu_e$ values has been also measured. An example of the field effect is shown in Fig. 4 for liquid Ar. A detailed comparison has been made further between the experimental results and the theoretical ones, from which it has been concluded that recombination...
in liquid and dense gaseous Ar, Kr and Xe, as well as in methane, is not a usual diffusion-controlled reaction.

![Electric field dependence of \( k_r \) and \( n \mu_e \) in liquid argon (T = 87 K, \( n = 2 \cdot 1 \times 10^{22} \text{ cm}^{-3} \)) (Shinsaka et al. 1988; Hatano 1994).](image)

Fig. 4. Electric field dependence of \( k_r \) (●) and \( n \mu_e \) (○) in liquid argon (\( T = 87 \text{ K} \), \( n = 2 \cdot 1 \times 10^{22} \text{ cm}^{-3} \)) (Shinsaka et al. 1988; Hatano 1994).

Theoretical investigations trying to explain the \( k_r \) deviation from \( k_D \) are summarised as follows:

1. A semi-empirical treatment taking both the diffusion controlled and electron-energy exchange controlled recombination processes into account (Warman 1983);
2. A Monte Carlo simulation with the parameter \( \Lambda/a \), where \( \Lambda \) is the mean free path of electrons and \( a \) is the reaction radius (Tachiya 1986, 1987a, 1987b);
3. A molecular dynamics simulation (Morgan 1986);
4. A fractal treatment (Lopez-Quintela et al. 1988; Mozumder 1990, 1993, 1995; Lopez-Quintela and Bujan-Nunes 1991);
5. A gas kinetic approach (Kaneko et al. 1988, 1990); and

Warman first proposed a theoretical formula for the recombination rate constant to explain the result of \( k_r \ll k_D \). In spite of many assumptions to derive the formula, the calculated value for liquid argon is in rather good agreement with the experimental one. For dense gaseous argon, however, the calculated value is far from the experimental one. Tachiya pointed out using a Monte Carlo method that if \( \Lambda/a \) is not negligible, the rate constant for bulk recombination deviates from \( k_D \). Experimental \( k_r \) values for liquid methane lie around the theoretical curve of his simulation which uses \( \Lambda/a \) only as a parameter. He also explained the effect of the field strength on \( k_r \). The values of \( k_r \) increase roughly in proportion to the field strength in the lower field strength region and form a peak at around the critical field strength. These results are explained in terms of the effect of the
field strength on the trajectory of electrons to be recombined. In the lower field region, the disentangling of random electron trajectories caused by the presence of the external electric field should increase $k_r$. In the field region higher than the critical field strength, the internal energy of an electron–ion pair (i.e. the energy in excess of the electron’s kinetic energy) decreases $k_r$.

4. Conclusions

A survey has been given of experimental studies of electron attachment and recombination in dense molecular media motivating developments of new theories on these processes. These studies have provided important information on the effect of van der Waals potentials and on the influence of surrounding medium molecules on these processes. They have also provided new insight into fundamental processes of phenomena in ionised gases and condensed matter.

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References


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