Contrib. Plasma Phys. **42** (2002) 6-7, 573−577

Low Energy Electron Collisions with Molecular Hydrogen

J. Tennyson[1], C. S. Trevisan

Department of Physics and Astronomy, University College London,
Gower St., London WC1E 6BT, UK.

Received 30 June 2001, in final form 31 January 2002

Abstract

We discuss the theory of electron-molecule excitation processes of importance in fusion plasmas. We consider elastic scattering, rotational, vibrational, and electronic excitation in turn and also dissociative attachment and impact dissociation.

1 Introduction

The collision of low energy electrons with diatomic molecule AB can lead to a number of possible processes. These include:

1. Elastic Scattering
$$AB + e^- \rightarrow AB + e^-$$
2. Rotational Excitation
$$AB(N'') + e^- \rightarrow AB(N') + e^-$$
3. Vibrational Excitation
$$AB(v''=0) + e^- \rightarrow AB(v') + e^-$$
4. Electronic Excitation
$$AB + e^- \rightarrow AB^* + e^-$$
5. Dissociative attachment
$$AB + e^- \rightarrow A^- + B \qquad \text{or} \qquad A + B^-$$
6. Impact dissociation
$$AB + e^- \rightarrow A + B + e^-$$

In the above we have taken low energy to be energies below the ionisation limit. All these processes can occur in cool hydrogen plasma, although they will have different importance because of (a) their likelihood for molecular hydrogen and (b) their effect on the properties of the plasma. We will consider the situation for each process in turn concentrating largely on theory. Experimental work on low energy electron collisions with hydrogen molecules forms an important part of a comprehensive review of electron diatomic molecule scattering cross sections by Brunger and Buckman [1]. Theoretical data, particularly for higher energy impacts with molecular hydrogen and its isotopomers, has recently been critically reviewed and compiled by Celiberto *et al* [2].

---

[1] Corresponding author: j.tennyson@ucl.ac.uk (J. Tennyson)

2 Elastic scattering

Elastic scattering may appear trivial as it involves no change in the internal energy state of the molecular target. However it does involve exchange of momentum between the colliding electron. Given that at most energies the elastic collisions dominate, it is thus the most important contributer to the thermalisation of hot electrons by collisions with molecules. Calculations and experiments for elastic cross sections, even differential ones which can then be used to give momentum transfer information, are in good agreement [3]. Calculations have the advantage that they provide information for all angles, something that is often difficult to obtain experimentally because of simple physical constraints on where one can place apparatus. For example cross sections for backward scattering, where the electron is reflected backwards by the target, are difficult to measure but result in a large transfer of momentum.

3 Rotational excitation

Hydrogen is one of the few molecules for which electron impact rotational excitation cross sections have been measured [4]. This is possible in H_2 because the (relatively) large rotational spacings mean that such experiments can be done with lower electron energy resolution than other, heavier molecules. There are a number of calculations of electron impact rotational excitation [4] [5] [6] which give reasonable agreement with experiment, in this case swarm results [7]. Rotational excitation cross sections are probably not of particular importance for present day models of cool hydrogen plasmas which do not work with rotational state distributions for the molecules.

4 Vibrational excitation

The low-energy electron impact vibrational excitation cross section for hydrogen has proved to be controversial. This is because cross sections inferred from swarm experiments have been consistently smaller than ones obtained from experiments performed using beams [8]. Theoretical studies using a variety of methods [5] [8] [9] strongly support the beam data and it is now generally accepted [1] [10] that these are indeed the correct cross sections.

5 Electronic excitation

Electron impact electronic excitation is a key process in the understanding of hydrogen plasmas. This is because electronic excitation often leads to dissociation (this is discussed separately below) and because emission from electronically excited states is the main spectroscopic handle on molecular hydrogen in plasmas. Data for interpreting these spectra requires vibrationally resolved electron impact electronic excitation cross sections for relatively high-lying electronic states of H_2. Particularly important are the Fulcher bands which involve transitions from triplet states which correlate with the H(1s) + H($n = 3$) dissociation limit. Experimentally there is essentially no data on electron impact excitation of vibrationally excited H_2, so it is important to develop reliable theoretical models for this problem.

Theoretical methods for treating electron impact dissociation broadly divide into two types: ‘low energy’ methods which treat several target states simultaneously in a close-coupling expansion, and 'high energy' methods of which the distorted wave approximation is probably the best. Celiberto *et al* [2] give a comprehensive compilation of high energy results.

The low energy methods, which include the R-matrix, the Kohn variational and the Schwinger method (see [11]), implicitly include multichannel effects and are capable of giving detailed descriptions of resonant processes. For example the complicated Feshbach resonances observed in electron H_2 (and HD and D_2) collisions have recently be satisfactorily explained using R-matrix calculations [12] [13]. This explanation meant abandoning conventional wisdom which associated a resonance with a particular 'parent' electronic excited state of the target [14].

The problem with close-coupling methods is that spurious effects are obtained unless all channels up to the energy of interest are included in the calculation. This makes such calculations increasingly difficult as the electron impact energy or the degree of target excitation increases. The distorted wave approximation does not suffer from this problem. However the simplification implicit in neglecting nearby channels can lead to (severe) underestimates of channel coupling effects and the method is probably not reliable for resonances.

There are some close coupling calculations available for electron impact excitation of the lower electronically excited states of H_2; those of Branchett and Tennyson [15] and Stibbe and Tennyson [13] are probably the most comprehensive. However so far none of these calculations have considered vibrational motion in detail. Conversely there are a number of calculations at the distorted wave, or similar level, which provide vibrationally resolved cross sections within a Franck-Condon-type treatment of the nuclear motion problem [6] [16] [17] [18]. Several of these calculations have also considered isotope effects, indeed there has been an attempt to derive scaling laws for this process [19], although these did not work as well for hydrogen as they did for the heavier molecules studied.

6 Impact dissociation

Low energy electron impact dissociation cross sections are difficult to measure as slow moving neutral particles are difficult to detect. Recently Stibbe and Tennyson [20] derived a new theoretical model for treating this process, based on the assumption that near threshold electron impact dissociation goes exclusively via electronic excitation to the first excited triplet state of H_2, the $b\ ^3\Sigma_u^+$ state:

$$e^- + \mathrm{H}_2(X\ ^1\Sigma_g^+) \rightarrow \mathrm{H}_2(b\ ^3\Sigma_u^+) + e^- \rightarrow \mathrm{H}(1s) + \mathrm{H}(1s) + e^-$$

This model gave good agreement with the limited available experimental data. Furthermore it predicted that rates of electron impact dissociation for thermal or near thermal electrons depend very strongly on the initial vibrational state of the molecule [21], so much so that this process could actually lead to a significantly altered (cooler) vibrational population of H_2.

Recently we [22] have studied differential cross section effects for electron impact dissociation of H_2. This required a reformulation of the problem and results in cross sections somewhat larger (by approximately 10%) than those predicted by Stibbe and Tennyson. Initial energy differential cross section studies suggested that upon dissociation the majority of the excess energy was carried away by the H atoms. However this work only considered dissociation from the vibrational ground state of H_2 and studies which explicitly consider vibrational excited molecules suggest that the energy distribution of dissociating H atoms may be more complicated. Preliminary results show that at higher vibrational levels, energy differential cross sections will follow the structure of the vibrational level involved. At lower projectile energies, the excess energy will continue to be carried away by the H atoms. But as the projectile energy increases, the population of H atoms carrying away most of the excess energy will decrease and slower H atoms may appear.

7 Conclusions

Electron collisions with molecules even at low energies are complicated by the plethora of different processes that can occur and different channels that can be excited. When, as is required for models of hydrogen plasmas, collisions with vibrationally excited targets are also considered, then one is almost totally reliant on theory for estimates of cross sections and/or rate constants. There are a number of processes for which theory can give excellent results for electron–H_2 collisions: elastic scattering, rotational excitation, vibrational excitation and low-lying Feshbach resonance being notable examples. However there are many other important situations where either the theory is known to need improving or there is insufficient experimental data to validate the theoretical results and hence the methods used.

References

[1] Brunger M.J., Buckman S.J., Phys. Rep. (2001), in press.

[2] Celiberto R., Janev R.K., Laricchuita A., Capitelli M., Wadehra J.M and Atems D.E., At. Data Nuc. Data Tables **77**, 161-213 (2001).

[3] Branchett S.E., Tennyson J., Morgan L.A., J. Phys. B: At. Mol. Opt. Phys., **24** (1991) 3479-3490.

[4] Morrison M.A., Crompton R.W., Saha B.C., Petrovic Z.L., Austr. J. Phys. **40** (1987) 239-281.

[5] Morrison M.A., Abdolsalami M., Elza B.K., Phys. Rev. A, **43** (1991) 3440-3459.

[6] Lee M.T., Michelin S.E., Brescansin L.M., Meneses G.D., Machado L.E., J. Phys. B: At. Mol. Opt. Phys. **26** (1993) L477-L481.

[7] England J.P., Elford M.T., Crompton R.W., Austr. J. Phys. **41** (1988) 573.

[8] Buckman S.J., Brunger M.J., Newman D.S., Snitchler G., Alston S., Norcross D.W., Morrison M.A., Saha B.C., Danby G., Trail W.K., Phys. Rev. Lett., **65** (1990) 3253-3256.

[9] Rescigno T.N., Elza B.K., Lengsfield III B.H., J. Phys. B: At. Mol. Opt. Phys. **26**(1993) L567-L573.

[10] Buckman S.J., Brunger M.J., Austr. J. Phys. **50** (1997) 483-509.

[11] Huo W.H., Gianturco, F.A. (eds.) *Computational Methods for electron-molecule collisions.* New York: Plenum (1995).

[12] Stibbe D.T., Tennyson J., Phys. Rev. Lett. **79** (1997) 4116-4119.

[13] Stibbe D.T., Tennyson J., J. Phys. B: At. Mol. Opt. Phys. **31** (1998) 815-844.

[14] Stibbe D.T., Tennyson J., J. Phys. B: At. Mol. Opt. Phys. **30** (1997) L301-L307.

[15] Branchett S.E., Tennyson J., Morgan L.A., J. Phys. B: At. Mol. Opt. Phys. **23** (1990) 4625-4639.

[16] Celiberto R., Rescigno T.N., Phys. Rev. A **47** (1993) 1939-1945.

[17] Lee M.T., Michelin S.E., Meneses G.D., Brescansin L.M., Machado L.E., J. Phys. B: At. Mol. Opt. Phys. **29** (1996) 2337-2346.

[18] Celiberto R., Laricchiuta A., Lamanna U.T., Janev R.K., Capitelli M., Phys. Rev. A **60** (1999) 2091-2103.
[19] Celiberto R., Capitelli M., Janev R.K., Chem. Phys. Lett. (1996) 575-580.
[20] Stibbe D.T., Tennyson J., New J. Phys. **1** (1998) 2.1-2.9.
[21] Stibbe D.T., Tennyson J., Astrophys. J., **513** (1999) L147-L150.
[22] Trevisan C.S., Tennyson J., J. Phys. B: At. Mol. Opt. Phys. **34** (2001) 2935-2949.