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Atom–Atom Collision Processes in Astrophysics: Theoretical Studies*

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Theoretical studies of atom–atom collision processes which may be relevant to the interpretation of astrophysical phenomena are reviewed. Work on excitation, ionization, and electron capture in atomic hydrogen by fast protons and He^+ ions is summarized. Processes involving slow collisions that are listed include radiative charge transfer and association, associative detachment, Penning ionization, spin-change, collision-induced deactivation, mutual neutralization, and rotational excitation.

Atom–atom collision processes which are relevant to astrophysical problems appear to occur either at thermal energies or at very high energies. Low-energy collisions require special considerations, but, with the exception of rearrangement processes, high-energy collisions can be described by the Born approximation. It follows that proton-impact cross sections for excitation and ionization of the target species are comparable to, but larger than, those for electron impact for equal *velocities* of the proton and the electron. Excitation and ionization by heavy particles other than bare nuclei is complicated by the possibility of excitation and ionization of the incident heavy particle; and collisions in which the incident particle and the target particle both undergo transitions may be more probable at high energies than collisions in which only one of the colliding pair undergoes a transition. However, high-energy neutral particles are rarely of interest in astrophysics since they are readily ionized, and the reverse process of charge transfer or electron capture is improbable. Although the high-energy behavior of the cross section for charge transfer

$$X^+ + Y \rightarrow X + Y^+$$

is still obscure (see Nikolaev 1965 and Bransden 1966 for reviews), it is clear that the cross section ultimately decreases rapidly. The expected rapid decrease may not emerge from laboratory investigations since capture of inner shell electrons is important up to very high energies (Mapleton 1966).

Except for bare nuclei, heavy particles can induce transitions involving a change of spin multiplicity. In such transitions the core of the heavy particle behaves as a spectator in the high-velocity limit, and the active electron may be regarded as a free electron. Explicit calculations for the reactions

$$H + He(1^1S) \rightarrow H + He(2^3S, 2^3P, 3^3P, 3^3D)$$

have been carried out by Bates and Crothers (1967).

Comprehensive accounts of atom–atom collisions are given in *Atomic and Molecular Processes* edited by Bates (1962), and a collection of more recent papers and reviews comprises *Atomic Collision Processes* edited by McDowell (1964).

HIGH-ENERGY COLLISIONS

Because of the occurrence of cosmic rays, high-energy collisions of protons and of neutral hydrogen atoms with hydrogen and possibly helium assume a special importance, and we present a brief discussion of the available data.

Comprehensive data are available only within the Born approximation. Calculations on a few processes have been performed using more refined approximations which are useful in assessing the accuracy and the range of validity of the Born approximation results (Bates 1959, 1961, Mittleman 1961, Bates and Williams 1964, Coleman and McDowell 1965, Lovell and McElroy 1965, Ingber 1965, Fulton and Mittleman 1965, Cheshire 1965, Coleman and McDowell 1966, Wilets and Gallaher 1966, Callaway and Dugan 1966, Basu, Sil, and Bhattacharya 1966, McCarroll and Salin 1966).

EXCITATION AND IONIZATION OF H BY H^+

Bates and Griffing (1953) (see also Bates 1958) have presented the results of Born approximation calculations of cross sections $Q(n_il_i; n_fl_f)$ for the excitation processes

$$H^+ + H(1s) \rightarrow H^+ + H(2s, 2p, 3s, 3p, 3d) \qquad (1)$$

and the ionization process

$$H^+ + H \rightarrow H^+ + H^+ + e. \qquad (2)$$

(See also Peach 1965.) For the ionization process, they present the velocity distributions of the ejected electron. The ionization cross section agrees closely with the measurements of Gilbody and Ireland (1964) above 40 keV, but lie above the measurements of Fite, Stebbings, Hummer, and Brackman (1960) below 40 keV. The cross section for excitation into the $2p$ state is about twice that measured by Stebbings, Young, Oxley, and Ehrhardt (1965) between 5 and 30 keV but falls below it for energies below 3 keV.

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At high energies (E measured in keV),

$$Q(1s;2s)\sim(11.1/E)[1-(7.8/E)]$$

and

$$Q(1s;2p)\sim(128/E)[\log E-1.185+(4.1/E)].$$

Cross sections are expressed in units of πa_0^2. Thus excitation of p states dominates in the asymptotic region. Cross sections for other values of n_i, l_i, n_f, and l_f may be derived from electron-impact cross sections (Bates and Griffing 1953, Carew and Milford 1963). May (1965a) has obtained a simple formula for excitation into all the substates corresponding to a particular value of n when n is large. He shows that

$$Q(1s;\sum_l nl)=[I(E)/n^3](1+O(n^{-2})),\qquad(3)$$

where $I(E)$ is given in Table I. Cross sections for excitation into all the discrete levels

$$\sum_{nl}Q(1s;nl)$$

have been calculated by Butler and Parcell (1965), and their results are reproduced in Table II.

Cross sections for transitions in which the target atom is excited have been computed by Carew and Milford (1963), who give results for the target atom in states with principal quantum numbers $n_i=2$, 3, 4, 5, and 10 for transitions such that $n_f-n_i=1$ or 2. With decreasing threshold energy, the cross-section maximum increases to lower energy and, as n_i increases, proton impact becomes more efficient than electron impact in causing transitions in the thermal energy range.

EXCITATION AND IONIZATION OF H BY H

Bates and Griffing (1954, 1955) (see also Bates 1958) have presented the results of Born approximation calculations of cross sections $Q(1s-n_1l_1;1s-n_2l_2)$ for the excitation processes

$$H(1s)+H(1s)\rightarrow H(n_1l_1)+H(n_2l_2)\qquad(4)$$

and for ionization processes

$$H(1s)+H(1s)\rightarrow H(n_1l_1)+H^++e\qquad(5)$$

$$H(1s)+H(1s)\rightarrow H^++e+H^++e.\qquad(6)$$

Table I. Values of the function $I(E)$ appearing in Eq. (3).

Impact energy E (keV)	$I(E)$
1.6	0.58
3.1	2.5
6.3	6.1
12.5	8.9
25	8.5
50	6.5
100	4.4
200	2.8

Table II. Cross sections Q in units of a_0^2 for $H^++H(1s)\rightarrow H^++H(nl)$.

Impact energy (keV)	$\Sigma_l\{Q(1s,2l)+Q(1s,3l)\}$	$\Sigma_nQ_l(1s;nl)$
6.24	2.26	2.53
7.71	2.49	2.83
9.76	2.67	3.04
12.74	2.74	3.12
17.35	2.75	3.15
25.0	2.58	2.95
39.0	2.24	2.57
69.4	1.72	1.95
156.1	1.08	1.23
277.6	0.74	0.83
624.5	0.41	0.44

At high impact energies, E (keV),

$$Q(1s-2s;1s-\sum)\sim4.3/E\qquad(7)$$

$$Q(1s-2p;1s-\sum)\sim21/E,\qquad(8)$$

where $\sum$ is the sum of all possible final states, including the continuum. For ionization at high energies,

$$Q(1s-C;1s-\sum)\sim128/E.$$

Collisions in which the incident atom remains in the $1s$ state contribute only about 13% of the total.

May (1965b) has derived further asymptotic formulas for

$$Q(1s-\sum_l nl;1s-1s)\quad\text{and}\quad Q(1s-\sum_l nl;1s-\sum),$$

showing that for large n they decrease as n^{-3}.

Bates and Griffing (1955) have obtained the velocity distributions of the electrons ejected in ionizing collisions of stationary hydrogen atoms by hydrogen-atom impact. To compute the velocity distributions of electrons ejected from the moving projectile atom, it is necessary to calculate also the angular distributions of the ejected electrons, and this calculation has been carried out by Dalgarno and Griffing (1958).

Collisions in which the target atom is excited have been investigated by Bouthilette, Healey, and Milford (1964) and collisions in which both the projectile and the target atom are excited by Pomilla and Milford (1966).

The charge transfer process

$$H+H\rightarrow H^++H^-$$

has been investigated by Mapleton (1965).

CHARGE TRANSFER OF H$^+$ IN H

Cross sections for electron capture by protons from atomic hydrogen

$$H^++H(1s)\rightarrow H(nl)+H^+$$

have been computed using the Brinkman–Kramer form of the Born approximation for final states up to $4f$ by Bates and Dalgarno (1953), and their work has been extended to higher states of excitation and to capture from excited atoms by Butler and Johnston (1964), by May (1964), by Hiskes (1965), and by May and Lodge (1965). The accuracy of the absolute cross sections is open to question, but the relative values for capture into different excited states appear to be satisfactory for impact energies above 40 keV (cf. Hiskes 1965). For large values of n, the cross sections decrease as n^{-3}.

Comparisons of different first-order approximations (cf. Bates 1962) have been made by Bates and Dalgarno (1952), Jackson and Schiff (1953), Bassel and Gerjuoy (1960), McCarroll (1961), and Mapleton (1962).

The cross section for capture into the $2p$ state is about twice that measured by Stebbings *et al.* (1965) between 5 and 30 keV, but falls below it for energies below 3 keV.

STOPPING POWER OF H⁺ IN H

The efficiency with which a beam of protons is slowed down in a gas of ground-state hydrogen atoms has been examined in detail by Dalgarno and Griffing (1955) using the Born approximation to the cross sections for the various processes. The mean energy expended in producing an ion pair in hydrogen gas has also been calculated as a function of impact energy (Dalgarno and Griffing 1958). The neutralization of the ion beam appears to extend the range of impact energies over which the mean energy per ion pair is essentially constant at a value of about 32 eV.

STOPPING POWER OF H⁺ IN AN H⁺, *e* PLASMA

The energy loss of fast protons in an ionized plasma has been calculated by Hayakawa and Kitao (1956) and by Butler and Buckingham (1962). The presence of free electrons in a gas increases markedly the rate of energy loss.

EXCITATION AND IONIZATION OF He BY H⁺ AND H

Theoretical calculations of the excitation and ionization of He are much less comprehensive than for H. The following processes have been studied:

$$\mathrm{H}^+ + \mathrm{He}(1^1S) \rightarrow \mathrm{H}^+ + \mathrm{He}(1s2p\,^1P)$$

(Moiseiwitsch and Stewart 1954, Bell 1961, Bell and Skinner 1962);

$$\mathrm{H}^+ + \mathrm{He}(1^1S) \rightarrow \mathrm{H}^+ + \mathrm{He}(1s3p\,^1P)$$

(Bell 1961, Bell and Skinner 1962);

$$\mathrm{H}^+ + \mathrm{He}(1^1S) \rightarrow \mathrm{H}^+ + \mathrm{He}^+(1s) + e$$

(Mapleton 1958, Peach 1965);

$$\mathrm{H}^+ + \mathrm{He}(1^1S)\,\mathrm{H}^+ + \mathrm{He}^+(nl) + e$$

(Dalgarno and McDowell 1955, Mapleton 1958);

$$\mathrm{H} + \mathrm{He}(1^1S) \rightarrow \mathrm{H}(\Sigma) + \mathrm{He}(1s2p\,^1P)$$

$$\mathrm{H} + \mathrm{He}(2^3S) \rightarrow \mathrm{H}(\Sigma) + \mathrm{He}(1s2p\,^3P)$$

$$\mathrm{H} + \mathrm{He}(2^3S) \rightarrow \mathrm{H}(\Sigma) + \mathrm{He}(1s3p\,^3P)$$

(Adler and Moiseiwitsch 1957);

$$\mathrm{H} + \mathrm{He}(1^1S) \rightarrow \mathrm{H}^+ + e + \mathrm{He}(\Sigma)$$

(Bates and Williams 1957).

The predicted ionization cross sections agree well with the measurements of Hooper, Harmer, Martin, and McDaniel (1962) at impact energies above 400 keV but lie above the experimental cross sections (Federenko, Afrosimov, Il'in, and Solov'ev 1960, Hooper *et al.* 1962) at lower energies.

CHARGE TRANSFER OF H⁺ IN He

Mapleton (1961, 1963) has used the Born approximation to calculate cross section for electron capture by protons from helium,

$$\mathrm{H}^+ + \mathrm{He}(1^1S) \rightarrow \mathrm{H}(nl) + \mathrm{He}^+(n'l')$$

for various excited states of the end products. The total charge-transfer cross section is in good agreement with the measured cross section (Stier and Barnett 1956, Barnett and Reynolds 1958) above 40 keV, and the cross section for capture into the $3s$ state of atomic hydrogen is in good agreement with that measured by Hughes, Dawson, Doughty, Kay, and Stiger (1966) above 100 keV, but lies above it at lower energies. Hughes *et al.* also obtained evidence suggesting that the cross sections for capture into the nth state of hydrogen decreases as n^{-3} for impact energies above about 20 keV. The theoretical cross sections for capture into the $2s$ and $2p$ states of hydrogen lie well above those measured by Pretzer, Van Zyl, and Geballe (1964), by Colli, Cristofori, Frigerio, and Sona (1962) and by Jaecks, Van Zyl, and Geballe (1965) at energies below 20 keV.

The electron capture process for the case when the hydrogen atom and helium atom are produced in their ground states has been studied using higher-order approximations by Bransden and Cheshire (1963), by Green, Stanley, and Chang (1965), and by Bransden and Sin Fai Laim (1966).

LOW-ENERGY COLLISIONS

Excitation by proton impact

The cross section for direct excitation by electron impact is broadly similar to that by proton impact if the electron and proton have the same velocity. The electron impact excitation cross section rises rapidly from threshold to a maximum, which occurs at an impact velocity corresponding to about twice the threshold energy, and then decreases asymptotically as $E^{-1} \ln E$

for optically allowed transitions, or as E^{-1} for optically forbidden transitions. Thus electron impact excitation is usually more efficient than proton impact excitation except when the threshold energy is only a small fraction of the thermal energy of the plasma.

An example of an excitation process for which proton impact is more efficient than electron impact is the $2s$–$2p$ transition in atomic hydrogen

$$H^{+}+H(2s_{1/2})\rightarrow H^{+}+H(2p_{1/2},\ 2p_{3/2}).$$

The threshold energies are, respectively, 0.0354 and 0.327 cm^{-1}. The reaction is important in reducing the intensity of the two-quantum emission from H($2s$).

The cross section has been calculated by Seaton (1955) using a partial wave analysis in which he ensured that no partial wave violated the conservation laws. The derived rate coefficients at 10 000° and at 20 000°K are reproduced in Table III. They are an order of magnitude larger than those for electrons. The charge transfer process

$$H^{+}+H(2s_{1/2})\rightarrow H(2p_{1/2},\ 2p_{3/2})+H^{+}$$

is negligible compared to the direct reaction (Boyd and Dalgarno 1958).

Collisions which lead merely to a redistribution of angular momentum

$$H^{+}+H(nl)\rightarrow H^{+}+H(nl')$$

will usually proceed very rapidly.

Similar reactions which may be of astrophysical importance are the proton impact excitation of molecular rotations

$$H^{+}+XY(j)\rightarrow H^{+}+XY(j').$$

The particular case

$$H^{+}+CN(j=0)\rightarrow H^{+}+CN(j=1)$$

has been investigated by Thaddeus and Clauser (1966) in connection with the cosmic microwave radiation at $\lambda=2.63$ mm (see also Field and Hitchcock 1966). Their calculations appear to be based upon an approximation analogous to the Bethe form of the Born approximation (cf. Seaton 1962). There occurs a strong long-range interaction between the proton and the permanent dipole moment of CN, and the derived cross section for 1-eV protons is about 10^{-12} cm^{2}. Thaddeus and Clauser suggest that the process may be important in HII regions.

Table III. Rate coefficient k for $H^{+}+H(2s)\rightarrow H^{+}+H(2p_{j})$.

T°K		10 000	20 000
k (cm^{3} sec^{-1})	$j=\frac{1}{2}$	2.5×10^{-4}	2.1×10^{-4}
	$j=\frac{3}{2}$	2.2×10^{-4}	2.2×10^{-4}

Table IV. Diffusion coefficients D^{+} of H^{+} in H.

T°K	1000	2000	5000	10 000	20 000	50 000
$D^{+}n(H)\times10^{17}$	1.7	2.6	4.6	7.1	11.1	20.0

Because of the strong coupling between different rotational levels during the collision, the cross sections for exciting higher rotational levels will be of comparable magnitude.

CHARGE TRANSFER

The symmetrical resonance charge-transfer process

$$H^{+}+H\rightarrow H+H^{+}$$

does not involve an electronic transition, and its cross section can be predicted reliably. At 1 eV the cross section is about 4×10^{-15} cm^{2} decreasing slowly with increasing energy (Dalgarno and Yadav 1953, Ferguson 1961, Peek 1966).

Resonance charge transfer significantly modifies the diffusion of H^{+} in H. Values of the ion diffusion coefficient have been calculated by Dalgarno (1961a), and they are reproduced in Table IV.

Asymmetric charge transfer processes

$$H^{+}+X\rightarrow H+X^{+}$$

involve an electronic transition, and they will, in most cases, proceed very slowly at thermal energies. Exceptions occur, and one such is

$$H^{+}+O(^{3}P)\rightarrow H+O^{+}(^{4}S),$$

which is accidentally resonant. Chamberlain (1956) has suggested that the reaction may affect the ratio of the 0 to 0^{+} densities in the Cassiopeia radio source.

There is no satisfactory theory of asymmetric charge transfer reactions, but an approximate analysis by Rapp (1963) of the measurements at high energies by Fite, Smith, and Stebbings (1962) shows that it behaves like a symmetric charge transfer reaction down to very low energies. The predicted cross section at 1 eV is 2×10^{-15} cm^{2}, a value consistent with the cross section of 8×10^{-15} cm^{2} at 1000°K derived by Hanson, Patterson, and Degaonkar (1963) from upper atmosphere data.

RADIATIVE CHARGE TRANSFER

Radiative charge-transfer processes in which a photon is emitted may proceed more rapidly than ordinary charge transfer at thermal energies. Calculations have been carried out for two simple cases using a theory in which the probability of a transition of the quasi-molecule formed by the colliding pair is integrated along the classical path (Bates 1951). The reactions which have been investigated are

$$He^{++}+H\rightarrow He^{+}+H^{+}+h\nu$$

(Arthurs and Hyslop 1957) and

$$He^{++}+He\rightarrow He^{+}+He^{+}+h\nu$$

(Allison and Dalgarno 1965). The first reaction has a rate coefficient of 1.5×10^{-13} sec^{-1} at 20 000°K and the second a rate coefficient of 4×10^{-15} cm^3 sec^{-1}.

RADIATIVE ASSOCIATION

Radiative association

$$X+Y\rightarrow XY+h\nu$$

provides a mechanism for the formation of molecules in gases at low densities. It may be described by a theory analogous to that appropriate to radiative charge transfer. Bates (1951) has computed the rate coefficient for

$$H^{+}+H\rightarrow H_2^{+}+h\nu,$$

obtaining a value of 5×10^{-18} cm^3 sec^{-1} at 1000°K increasing to 4×10^{-16} cm^3 sec^{-1} at 20 000°K. Bates also tabulates the rate coefficient for the free–free transition

$$H^{+}+H\rightarrow H^{+}+H+h\nu.$$

For the reactions

$$C+H\rightarrow CH+h\nu$$

$$C^{+}+H\rightarrow CH^{+}+h\nu$$

Bates (1951) has given tentative estimates of 2×10^{-18} cm^3 sec^{-1}, but he notes that the rate coefficient of the former may be 6×10^{-18} cm^3 sec^{-1} if the carbon atoms are all in the $^3P_0$ state, and that the rate coefficient of the latter may vanish if the carbon atoms are all in the $^2P_{1/2}$ state.

The rate of formation of HeH$^+$ has not been calculated, though the molecule undoubtedly exists (Michels 1966, Harris 1966).

The free-bound absorption

$$H+H+h\nu\rightarrow H_2'$$

has been investigated by Erkovich (1960), Soshnikov (1964), and Solomon (1964) for the transition $(1s\sigma2p\sigma\,{}^3\Sigma_u{}^{+}-1s\sigma2s\sigma\,{}^3\Sigma_g{}^{+})$. The process does not seem to be a significant source of absorption.

The radiative association of two hydrogen atoms

$$H+H\rightarrow H_2+h\nu$$

is a very slow process since the stabilizing transition is highly forbidden. Malville (1964) has given an estimate of 4×10^{-27} cm^3 sec^{-1} at 100°K for its rate coefficient.

COLLISION-INDUCED RADIATIVE DEACTIVATION

Allison and Dalgarno (1963) have calculated the rate coefficient for

$$H^{+}+He(2^1S)\rightarrow H^{+}+He(1^1S)+h\nu.$$

Because of the large polarizability of He(2^1S), the reaction proceeds quite rapidly with a rate coefficient of 10^{-11} cm^3 sec^{-1} at 20 000°K.

A similar study of the reaction

$$He(1^1S)+He(2^1S)\rightarrow He(1^1S)+He(1^1S)+h\nu$$

has been completed by Allison, Browne, and Dalgarno (1966), who obtain a rate coefficient of 3×10^{-14} cm^3 sec^{-1} at 20 000°K.

ASSOCIATIVE DETACHMENT

Associate detachment

$$X+Y^{-}\rightarrow XY+e$$

is an efficient mechanism for the destruction of negative ions. It may be regarded as proceeding through the formation of a quasi-molecule XY$^-$ which can undergo autodetachment. Since the mean time for autodetachment is usually much less than the mean time the nuclei remain in the autodetaching region, the probability of autodetachment is high. This simple picture led Dalgarno (1961a) to advocate a rate coefficient of up to 10^{-9} cm^3 sec^{-1} for

$$H+H^{-}\rightarrow H_2+e.$$

Developments in the theory of resonating states should yield a more precise estimate (see in particular Bardsley, Herzenberg, and Mandl 1966).

The process is also of interest in that it leads to a production of hydrogen molecules (McDowell 1961).

MUTUAL NEUTRALIZATION

Mutual neutralization

$$X^{+}+Y^{-}\rightarrow X+Y$$

usually proceeds rapidly at thermal energies because of the long range attraction in the initial channel and because intersecting potential energy surfaces are available connecting the initial and final channels. (Bates and Massey 1954, Bates and Boyd 1956). The case

$$H^{+}+H^{-}\rightarrow H+H$$

has been studied in detail by Bates and Lewis (1955), who have shown that the rate coefficient may be as large as 10^{-7} cm^3 sec^{-1} and varies approximately as $T^{-1/2}$.

PENNING IONIZATION

Thermal ionization

$$X+Y\rightarrow X+Y^{+}+e$$

can also occur efficiently in many instances because of the existence of intersecting potential energy surfaces (Bates and Massey 1954). The colliding systems may become bound forming XY$^+$, a process known as associative ionization. The processes are analogous to associative detachment in that a radiationless transition (autoionization) occurs.

Quantal studies have been made by Katsuura (1965), Smirnov and Firsov (1965), Mori (1966), Sheldon (1966), and Bates, Bell, and Kingston (1967). Bates *et al.* have emphasized that the long-range interactions can lead to large rate coefficients. For

$$\mathrm{H}(2s, 2p)+\mathrm{H}(2s, 2p)\rightarrow\mathrm{H}(1s)+\mathrm{H}^{+}+e$$

Bates *et al.* estimate a rate coefficient at temperature T of $2\times10^{-8}\ T^{-1/6}$ cm³ sec⁻¹ and for

$$\mathrm{He}(2^{3}S)+\mathrm{He}(2^{3}S)\rightarrow\mathrm{He}(1^{1}S)+\mathrm{He}^{+}+e,$$

a rate coefficient of $7\times10^{-10}\ T^{1/6}$ cm³ sec⁻¹. They note that Penning ionization processes, which can take place only through exchange and which involve the transfer of an electron between compact orbitals around unlike centers, such as

$$\mathrm{He}(2^{3}S)+\mathrm{Ar}(^{1}S)\rightarrow\mathrm{He}(1^{1}S)\mathrm{Ar}^{+}+e,$$

will be less efficient. Rate coefficients for the ionization of alkali atoms by metastable inert gas atoms have been computed by Sheldon (1966) and for the ionization of Li and Cs by Smirnov and Firsov (1965). The values are of the order of $10^{-9}-10^{-10}$ cm³ sec⁻¹.

EXCITATION BY NEUTRAL HYDROGEN ATOM IMPACT

The excitation of rotational levels of molecular hydrogen by the impact of hydrogen atoms is an important cooling mechanism in interstellar space. Cross sections for

$$\mathrm{H}+\mathrm{H}_2(j=0)\rightarrow\mathrm{H}+\mathrm{H}_2(j=2)$$

have been calculated by Takayanagi and Nishimura (1960) using an approximate version of the distorted wave method. The distorted wave method has been applied without further approximation by Dalgarno, Henry, and Roberts (1966) with results in close agreement with the earlier calculations. Their cooling rates are reproduced in Table V.

Recently Allison and Dalgarno (1967) have solved the set of coupled equations that describes the collision, obtaining cross sections which are somewhat lower at high temperatures than those derived from the distorted-wave approximation. The corresponding rate coefficient is included in Table V. However, the major uncertainty in the predicted cooling rates lies in the interaction potential between H and H_2.

Takayanagi and Nishimura (1960) and Dalgarno *et al.* (1966) have also tabulated excitation rates for other rotational transitions in H_2 and D_2.

The excitation of H_2 by H_2

$$\mathrm{H}_2(j=0)+\mathrm{H}_2(j=0)\rightarrow\mathrm{H}_2(j)+\mathrm{H}_2(j')$$

is less important. The most accurate cross sections are those computed by Allison and Dalgarno (1967).

Takayanagi and Nishimura (1960) have roughly estimated the rate coefficient for excitation of the 0–1 rotational transition in CH, CN, and OH to be 3.5×10^{-10} cm³ sec⁻¹, corresponding to a cross section of about 10^{-15} cm².

Table V. Rate coefficient $\mathrm{H}-\mathrm{H}_2(j-j')$ (cm³ sec⁻¹).

T°K	0–2		1–3	2–4
	(a)	(b)	(a)	(a)
20	3.4(−23)	4.5(−23)		
30	2.8(−19)	4.0(−19)	7.21(−25)	
40	2.8(−17)	3.5(−17)	1.3(−21)	
50	4.4(−16)	5.1(−16)	1.3(−19)	4.3(−23)
60	2.9(−15)	3.1(−15)	2.7(−18)	3.1(−21)
80	3.2(−14)	3.1(−14)	1.3(−16)	6.8(−19)
100	1.4(−13)	1.3(−13)	1.5(−15)	1.9(−17)
200	3.8(−12)	3.1(−12)	2.6(−13)	2.1(−14)
300	1.4(−11)	1.1(−11)	1.9(−12)	2.9(−13)
500	5.3(−11)	3.7(−11)	1.3(−11)	3.4(−12)
1000	2.2(−10)		7.8(−11)	3.4(−11)
2000	7.1(−10)		3.1(−10)	1.7(−10)
3000	1.4(−9)		6.4(−10)	3.7(−10)
4000	2.2(−9)		1.0(−9)	6.2(−10)
5000	3.1(−9)		1.5(−9)	9.2(−10)

[a] From Dalgarno, Henry, and Roberts (1966).
[b] From Allison and Dalgarno (1967).

SPIN-CHANGE PROCESSES

Purcell and Field (1956) drew attention to the role of the spin-change process

$$\mathrm{H}(F=0)+\mathrm{H}\rightarrow\mathrm{H}(F=1)+\mathrm{H}$$

in controlling the spin population of atomic hydrogen and gave a rough estimate of its cross section. The process has been further studied by Dalgarno (1961b) and by Dalgarno and Henry (1964) using a theory which assumes the collision to be elastic and which ignores the effect of molecular rotation during the collision. The derived cross sections, averaged over a Maxwellian velocity distribution, oscillate about a value of 8×10^{-15} cm² for $T<100$°K and decrease slowly at higher temperatures.

A similar process

$$\mathrm{O}(^{3}P_{J})+\mathrm{H}\rightarrow\mathrm{O}(^{3}P_{J'})+\mathrm{H}$$

was advanced by Burgess, Field, and Michie (1960) as a possible cooling mechanism in interstellar space, and Dalgarno and Rudge (1964) proposed the additional mechanisms

$$\mathrm{C}^{+}(^{2}P_{J})+\mathrm{H}\rightarrow\mathrm{C}^{+}(^{2}P_{J'})+\mathrm{H}$$

$$\mathrm{Si}^{+}(^{2}P_{J})+\mathrm{H}\rightarrow\mathrm{Si}^{+}(^{2}P_{J'})+\mathrm{H},$$

giving a rough estimate of the cross section. Smith (1966b) has computed the corresponding cooling rates, and he concludes that the O–H reaction is more efficient than the C^+–H and Si^+–H reactions (despite the long-range attraction), and that below 300°K the O–H reaction is a more efficient cooling mechanism than excitation of the rotational levels of H_2 by hydrogen atom impact.

The theoretical description used by Smith is an extension of that presented by Dalgarno and Rudge (1965) for collision-induced changes in the hyperfine structure of alkali metal vapors, and it may not be adequate for collision-induced changes in fine structure (cf. Nikitin 1965, Callaway and Bauer 1965).

QUENCHING COLLISIONS

The quenching of radiation through the destruction process

$$X+Na(^2P_{1/2})\rightarrow X+Na(^2S_{1/2})$$

has been studied theoretically by Nikitin and Bykhovskii (1964), but the lack of adequate wave functions for the quasi-molecule XNa has prevented quantitative predictions. For inert gas atoms, the measured cross sections are about 10^{-16} cm^2. Larger cross sections occur when X is a diatomic molecule (cf. Starr and Shaw 1966).

CHEMICAL REACTIONS

Herzberg (1955) has listed a number of exothermic reactions which produce molecular hydrogen:

$$CH^+ + H \rightarrow H_2 + C^+,$$

$$CH + H \rightarrow H_2 + C,$$

$$NH + H \rightarrow H_2 + N,$$

$$OH + H \rightarrow H_2 + O,$$

and Stecher and Williams (1967) have listed other exothermic reactions which produce CH, OH, NH, CN, CO, and N_2. It is conventional practice to adopt the Arrhenius form for the rate coefficients

$$K = A \exp(-K/kT)$$

and to assume that the activation energy E is given by

$$A = 0.055D,$$

where D is the dissociation energy of the initial molecule (Polanyi 1962). A review of some of the reactions involving atomic hydrogen has been presented by Kaufman (1964). Recent work on OH radical reactions is described by Skinner and Ringrose (1965) (see also Carroll and Salpeter 1966).

TRANSPORT PROPERTIES

The thermal conductivity and the viscosity of atomic hydrogen have been calculated to high accuracy by Dalgarno and Smith (1962) at high temperatures and by Buckingham, Fox, and Gal (1965) at low temperatures. The diffusion coefficient of protons in atomic hydrogen gas is given in Table IV. Formulas for the transport coefficients appropriate to a fully ionized plasma have been derived by Spitzer (1956) (see Devoto 1966).

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