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Dissociation of Hydrogen Molecules by Vibrational Excitation and Three-Body Recombination Coefficient. II

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The recombination of two hydrogen atoms in the presence of a third in a thermal collision is considered, the principle of detailed balance being used to obtain the three-body coefficient C_3 from the cross section σ_2 of the reverse, dissociation process. This cross section is calculated by a method developed previously which depends on correcting the Born approximation by means of the exact one-dimensional problem. We consider the case when the molecule is formed in a highly excited vibrational state of the electronic ground state and the excess energy of several kT goes into translational energy of the third atom. The three-body coefficient in this case is of order 3×10^{-36} cm^6 sec^{-1}, which is still much smaller than the empirical values. Some estimate is made of the validity of the correction method.

The excitation and de-excitation of the first vibrational state of hydrogen by collisions with protons is investigated, and it is found that an excited molecule requires 10^3 to 10^4 thermal collisions to lose its excitation; this is roughly of the correct order of magnitude for such processes.

I. INTRODUCTION

Chemical recombination reactions typified by the process

$$H+H+X\rightarrow H_2+X^*, \qquad (1)$$

where H is a hydrogen atom, and X is an atom or molecule, are of importance in the upper atmosphere and perhaps also in chemical kinetics, but have not been studied extensively theoretically. There are three basic kinds of mechanism, namely:

(a) The two hydrogen atoms come together in the repulsive $^3\Sigma$ electronic state of the molecule and give up their excess electronic energy to X.

(b) They may come together in the vibrational continuum of the normal $^1\Sigma$ electronic state and transfer their excess vibrational energy to X.

(c) They may come together with a large orbital angular momentum, and transfer some of this rotational energy to X.

In each case different mechanisms are possible depending on the mode of excitation of X. In case (a), the most probable process is one involving the electronic excitation of X, which has been studied recently by Moses and Wu.[1] In thermal energy collisions electronic processes are adiabatic, and in case (b) the transfer of vibrational energy to the translational excitation of X has been studied by the present writer.[2] The probability of the dissociation of H_2 from the vibrational ground state by excitation into the vibrational continuum of the normal electronic state in collision with a hydrogen atom (Section VI) and a proton (Section II) was calculated, and the probability of (1) estimated from this by using the principle of detailed balance; the resulting three-body recombination coefficient was found to be of the order 10^{-43} cm^6 sec^{-1}.

Experiments[3] give the value $C_3\sim3\times10^{-32}$ cm^6 sec^{-1}. This seems to be very large, since even a gas kinetic value for the dissociation cross section σ_2 would only correspond to $C_3\sim10^{-35}$ cm^6 sec^{-1}. In any case, the difference between theoretical and experimental values is so large that it is desirable to examine other processes theoretically. A process similar to the one considered previously,[2] in which the final state of the molecule is not the vibrational ground state but rather a highly excited vibrational state, may be much more probable as the energy to be transferred is then much smaller. This is supported by observations that in the afterglow in nitrogen in which there is no electrical excitation and the bands presumably arise from molecules resulting from recombinations, bands from highly excited vibrational levels are observed. In the present work, an estimate has been made of the probability of the transfer of an amount of vibrational energy of the order of the thermal energy in collisions of type (1), where X is a proton or hydrogen atom. The method of calculation is that described previously.[2]

The cross section for excitation of the first vibrational state from the ground state is calculated, and also that for the $v=13$ to $v=14$ excitation. The first of these gives information on the probability that a thermal collision of a proton with a vibrating molecule de-excites the vibration, while the second cross section would be expected to be of the same order as the cross section σ_2 of the reverse process of (1), as the energy transfer and other conditions are rather similar.

II. THREE-BODY COEFFICIENT

We consider transitions between a bound state Q of the molecule of binding energy Δ_Q, and a free state P in which the two atoms fly apart with relative kinetic energy $E_p=\hbar^2p^2/2M_0(M_0=\frac{1}{2}M_H)$; the third body (proton) has initially momentum $\hbar\mathbf{k}_0$, finally $\hbar\mathbf{k}_f$, all in the center-of-mass system in which its reduced

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[1] H. E. Moses and T. Y. Wu, Phys. Rev. **83**, 109 (1951), Appendix 5.

[2] E. Bauer, Phys. Rev. **84**, 315 (1951).

[3] H. J. Schumacher, *Chemische Gasreaktionen* (Theodor Steinkopff Verlag, Leipzig, 1938), p. 324.

mass is $M_A=\frac{2}{3}M_{\rm H}$. The interaction between the molecule in the $P\rightarrow Q$ transition and the atom is taken to be[4,2]

$$V_{QP}(r)=Ze^2\frac{\eta_{QP}(0.42)}{\rho_0}\Lambda_\mu\frac{e^{-\mu r}}{r}, \tag{2}$$

where $\Lambda_\mu=(1-\frac{1}{2}\mu\partial/\partial\mu)$, $\rho=$nuclear separation$=\rho_0+\eta$, $\rho_0=$equilibrium nuclear separation$\simeq$0.75A, $Z=1.115$, and $\mu=2.332$.

The cross section σ_2 for the $(Q, 0)\rightarrow(P, f)$ transition is obtained by using the Born approximation and correcting it by multiplying by ζ^2, the square of the ratio of exact to sine wave matrix element of the interaction in one dimension, as once again the Faxén-Holtsmark method is not practicable because of the large number of phases required. The resulting expression for σ_2 is[2]

$$\begin{aligned}
&\sigma_2(\Delta_Q, k_0)=\int dE_p\cdot\eta_{QP}{}^2(0.42/\rho_0)^2\chi(k_0, k_f(p), p)\zeta^2,\\
&\chi=\pi\alpha_0{}^2(2/\mu)^2A,\quad A=[Y+Y^2+\tfrac{1}{3}Y^3]_{Y+}^{Y-},\\
&Y_\pm=1/(1+X_\pm),\quad X_\pm=[(k_0\pm k_f)/\mu]^2,\\
&\alpha_0=Ze^2/\hbar v_0=ZM_Ae^2/\hbar^2k_0.
\end{aligned}\tag{3}$$

χ is a factor determined by the contribution of the translational motion to the cross section, evaluated by the use of Born's approximation. The state P is in the continuum, and is represented by a wave function normalized per unit energy range, so that integration over E_f is necessary. The range of integration is determined by energy conservation—

$$\hbar^2/2M_A(k_0{}^2-k_f{}^2)=\Delta_Q+(\hbar^2p^2/2M_0), \tag{4}$$

and goes from $p=0$ to the value corresponding to $k_f=0$.

The correction factor ζ is evaluated as before[2] using as "exact" wave functions Bessel functions of order chosen to represent the correct classical turning point of the motion, X_1. This should be a good approximation, since most of the contribution to the matrix element comes from the region near X_1. Some values of ζ are given in Table I, and some discussion of the method is given in Sec. IV.

To evaluate η_{QP}, we suppose that the internuclear potential (a function of ρ) may be represented by a square well of depth D (the dissociation energy) and width l_1. Then we define

$$\begin{aligned}
\hbar^2Q^2/2M_0&=D-\Delta_Q,\\
\hbar^2P^2/2M_0&=D+\hbar^2p^2/2M_0.
\end{aligned}\tag{5}$$

In order to have a bound state Q, it is necessary that

$$Ql_1=(n+\tfrac{1}{2})\pi,\quad n \text{ an integer}, \tag{6}$$

and taking $\Delta_Q=kT$ (at 300°K), $l_1=1.91a_0$, we have $Ql_1=10.5\pi$, and the wave functions are

$$\begin{aligned}
\psi_Q(\rho)&=N_Q\cos[Q(\rho-\rho_1)-\pi/4],\\
N_Q&=[2/(l_1+1/Q)]^{\frac{1}{2}}\simeq(2/l_1)^{\frac{1}{2}},\\
\psi_P(\rho)&=N_P\cos[P(\rho-\rho_3)-\pi/4],\\
N_P&=(1/\hbar)(2M_0/\pi P)^{\frac{1}{2}}.
\end{aligned}\tag{7}$$

ψ_Q is normalized to unity within the well, which goes from $\rho_1\leqslant\rho\leqslant\rho_1+l_1$, while ψ_P is normalized per unit energy range. The evaluation of $\eta_{QP}{}^2$ is straightforward; we are only interested in values $E_p\lesssim kT$, and there $\eta_{QP}{}^2$ has practically the same value as for $p=0$, namely, if we put $\rho_1\simeq\rho_0$,[4a]

$$\eta_{QP}{}^2=M_0l_1{}^4/4\pi\hbar^2Ql_1. \tag{8}$$

In evaluating σ_2 it is convenient to change the integration over E_p into one over $E_f=\hbar^2k_f{}^2/2M_A$, and the result is

$$\sigma_2(\Delta_Q=kT;\,E_0'=4.5kT)\simeq6\cdot10^{-19}\ \text{cm}^2.$$

E_0' is given in the "laboratory" system of coordinates in which the center of mass of the molecule is at rest, rather than in the relative system of coordinate in which the calculation is carried out; thus $E_0'=\frac{3}{2}E_0$.

Of more interest than σ_2 is the three-body recombination coefficient $C_3(E_p, E_f)$ which gives the probability that two hydrogen atoms moving with relative kinetic energy E_p will recombine on colliding with a proton whose kinetic energy is E_f relative to the center of mass of the system. C_3 may be found in terms of σ_2 by means of the principle of detailed balancing; if we write

$$\sigma_2(\Delta_Q, k_0)=\int_0^{p_{\max}}pdp\Sigma(k_0, k_f(p), p), \tag{3$'$}$$

then, neglecting angular factors,

$$\begin{aligned}
C_3(E_p, E_f)=\pi h\frac{G_{\rm H_2}}{G_{\rm H}{}^2}\frac{G_{X^*}}{G_X}\frac{M_0\rho_0{}^2}{M_A{}^2}\frac{1}{pk_f}\int_0^{k_2}\\
\times\Sigma(k_0, k_f(p), p)k_0{}^3dk_0,
\end{aligned}\tag{10}$$

where k_2 is determined by conservation of energy [Eq. (4)]. The G's are statistical weights, $G_{\rm H}=2$, $G_{\rm H_2}=1$, $G_X=G_{X^*}$. If $E_p=kT$ and E_f', the kinetic energy of the proton relative to the molecule, is $\frac{3}{2}kT$, we find $C_3\simeq3\times10^{-37}$ cm^6 sec^{-1}.

III. THE EXCITATION OF SOME DISCRETE VIBRATIONAL STATES

It is of some interest to calculate the cross section for transitions between two discrete vibrational states a, b of the electronic ground state in slow collisions with a proton. For a transition $(k_0, a)\rightarrow(k_f, b)$,

$$\sigma_{ab}=\pi\alpha_0{}^2|\eta_{ab}|^2(2/\mu)^2A\zeta^2(0.42/\rho_0)^2, \tag{11}$$

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[4] T. Y. Wu, Phys. Rev. **71**, 111 (1947).

[4a] This approximation is very rough, but if one describes the inter-nuclear potential by a Morse function one gets approximately the same result.

TABLE I. The correction method for protons.

	E_0'(xv)	α_0	α_f	X_1^0/a_0	X_1^f/a_0	ν_0	ν_f	ζ	σ(cm^2)	$\sigma/\sigma_{\max}$
A	Large	1/137	1/137	1	1	$\frac{1}{2}$	$\frac{1}{2}$	1		1
B	165 ev	13.7	14	0.212	0.218	21.2	21.5	0.152	3×10^{-25}	5
B	41.5 ev	27.5	30	0.522	0.572	25.8	26.2	0.035	2×10^{-25}	0.4
C	1.65 ev	137	192	1.66	1.93	16.6	13.8	0.0075	10^{-19}	0.04
C	1.05 ev	171	354	1.84	2.45	14.7	9.5	0.0039	2×10^{-20}	0.005
D	6 kt	450	900	2.65	3.20	8.1	4.9	0.0035	8×10^{-18}	0.06
E	3.9 kt	560	1200	2.81	3.44	6.9	3.95	0.0026	3×10^{-19}	0.03
F	3.9 kt	560	560	2.81	2.81	6.9	6.9	0.0026	3×10^{-17}	0.05

[a] *A* = Very high energies, *B* = Dissociation from the ground state; energy transfer 4.5 ev (reference 2); $\sigma=\sigma_2$. *C* = Excitation of the first vibrational state; energy transfer 0.5 ev (Sec. III); $\sigma=\sigma_{01}$. *D* = Transition $v=13$ to 14; energy transfer 621 cm$^{-1}\simeq 3kT$ (Sec. III); $\sigma=\sigma_{13\rightarrow14}$. *E* = Dissociation from a highly excited vibrational state; energy transfer $2kT$ (Sec. II); $\sigma=\sigma_2$. *F* = Elastic collision, quoted for comparison with *E*. E_0' = kinetic energy of the proton relative to the center of mass of the molecule. α_{01}, α_f = coupling constants $Ze^2/\hbar v$ for initial and final states. x_1^0/a_0, x_1^f/a_0 = classical closest distance of approach for initial and final states measured in units of the Bohr radius $a_0=\hbar^2/me^2\simeq0.529\times10^{-0}$ cm. ν_0, ν_1 = order of the Bessel function in the "exact" one-dimensional evaluation. ζ = correction factor: ratio of "exact" to sine-wave matrix element of the interaction (2) in one dimension. σ = cross section. $\sigma_{\max}$ = maximum value, defined by Eq. (13).

and detailed balancing gives

$$\sigma_{ba}=(E_0/E_f)\sigma_{ab}. \tag{12}$$

The $v=0\rightarrow v=1$ transition is of some practical interest, as the probability of de-excitation of the first vibrational state of molecules may be determined experimentally from measurements on the dispersion of high frequency sound waves in gases.[5] At thermal energies $\sigma_{10}\simeq10^{-19}$ cm^2, so that one in 10^3 to 10^4 collisions with a proton should de-excite the vibration. The vibrational dispersion has not been observed in hydrogen where the vibrational frequency is relatively large, but for other gases generally one in 10^3 to 10^6 collisions with gas molecules produces de-excitation.

The cross section for the transition between the two highest observed vibrational levels, $v=13$ and 14[6] has also been worked out. Here the energy difference is 621 cm$^{-1}\simeq 3kT$. Instead of calculating $\eta_{vv'}$ one works out $\langle v|d/d\eta|v'\rangle$, using wave functions derived from a Morse potential that fits the dissociation energy and vibration frequency for low excited states, as this has been found much easier than to evaluate $\eta_{vv'}$ directly.[7] From the wave equation one obtains readily the relation

$$\eta_{vv'}=\frac{\hbar^2}{M_0(E_v-E_{v'})}\langle v|d/d\eta|v'\rangle,$$

and it is found that

$$\sigma_{13\rightarrow14}(E_f'=\tfrac{3}{2}kT)\simeq8\times10^{-18}\text{ cm}^2.$$

The large value as compared with σ_{01} arises physically from the relatively small energy transfer in the collision. $\sigma_{13\rightarrow14}$ is about ten times as big as σ_2 of the previous section; the difference probably comes mostly from the different vibrational wave functions used in the two cases. If one uses $\sigma_{13\rightarrow14}$ instead of σ_2 in the relation of detailed balance (10), one obtains $C_3\simeq3\times10^{-36}$ cm^6 sec^{-1}, which is still much smaller than the experimental values.

IV. MAXIMUM VALUES FOR CROSS SECTIONS

It is well known that the conservation of particle flux sets maximum values to the partial cross sections of given orders.[8] In the present case the use of Wu's argument[4] gives

$$\sigma_{ab}\leqslant4\pi R^2(0.42\eta_{ab}/p_0)^2. \tag{13}$$

For low energy collisions of protons the range R of the interaction may be taken as the classical closest distance of approach, X_1. Some values of $\sigma/\sigma_{\max}$ are given in Table I.

V. DISCUSSION OF THE CORRECTION METHOD: PROTON AS THIRD BODY

It is not possible to say anything very definite about the method of correcting the Born approximation by multiplying the cross section by ζ^2, where ζ is the ratio of exact to sine-wave matrix elements of the interaction in one dimension, but several remarks may be made.

(a) For coupling constants $\alpha<1$ we find $\zeta\sim1$, so that the method is satisfactory for sufficiently high energies.

(b) At low energies the correction will become better as fewer phases are required; in fact the method should be satisfactory if only the S-wave had to be considered. (However, the reason for using the method at all is that in all practical cases a large number of phases is required.)

(c) As a test of the method, the calculated cross sections are compared with the maximum cross sections of the previous section in Table I. At energies less than 80 ev all calculated cross sections lie well within the maximum permissible values, while the uncorrected Born approximation would be far in excess of the limit.[9]

(d) ζ is not a very critical function of the different parameters.

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[5] W. T. Richards, Revs. Modern Phys. **11**, 33 (1939).

[6] H. Beutler, Z. Phys. Chemie, **B27**, 287 (1934).

[7] T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Edward Brothers, Ann Arbor, Michigan, 1946), second edition, p. 73. Strictly speaking, the use of a Morse potential is not justified for these highly excited states; nevertheless, one would expect to get the correct order of magnitude for $\eta_{vv'}$.

[8] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), Chapter 8.

[9] For $1<\alpha_0<20$ the cross section calculated by this method exceeds the maximum by a factor up to 15. This particular energy range is not very interesting, corresponding to 30,000 ev$>E_0'>$80 ev. We may estimate that the correction leads to an uncertainty of perhaps a factor 100 in the cross section.

VI. THE CASE OF HYDROGEN ATOMS AS THIRD BODY

To the present approximation,[2] the difference between protons and hydrogen atoms is that the orbital electron produces an (attractive) screening field; electronic transitions are of course not considered here. The effect of the screening field is to make the total interaction with a hydrogen molecule weakly attractive for separations greater than $1.3a_0$, with a maximum depth of $-0.02e^2/a_0$ at $r=1.8a_0$; at smaller distances ($r\lesssim a_0$) the effect of the screening field is negligible, and the field is again repulsive.

In the case considered previously[2] the attractive potential is of no importance at the lower energies ($\sim$5 ev), although it does give a contribution at large energies. In the present case the closest distance of approach for protons is greater than $1.3a_0$, so that the screening field affects the one-dimensional matrix element very strongly. If the correction method is applied in the usual way, one finds a correction factor $\zeta\sim(+)10^{-3}$ to 10^{-2} for the $(0\rightarrow1)$ transition, i.e., for energies $\gtrsim1$ ev, and $\zeta\sim(-)10^{-2}$ for thermal energies (dissociation and elastic scattering). The change of sign of ζ arises from the change of sign of the potential with increasing distance. The calculation is relatively difficult, because it is impossible to use the Bessel function method and the much more tedious WKB method must be used instead. The result is that for thermal energies, elastic scattering cross sections and three-body coefficients are increased by a factor of ten over those for protons, while the $(0\rightarrow1)$ cross sections are not changed in their order of magnitude, although the change of sign of ζ with the corresponding zero in the cross section falls not far above the threshold of the $(0\rightarrow1)$ transition.

The conclusion is that we may perhaps accept the thermal energy cross sections very tentatively: the three-body coefficient for two hydrogen atoms recombining in the presence of a third is of order 3×10^{-36} cm^6 sec^{-1}, while the cross section for the elastic scattering of a hydrogen atom of energy $\frac{3}{2}kT$ by a hydrogen molecule is of order 5×10^{-15} cm^2. Thus we see that it is still not possible to understand the experimental value of the three-body coefficient; electronic resonance processes are hardly likely as most other gases (nitrogen, halogens) give similar values for C_3 as does hydrogen.[3]

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An Investigation of Alpha-Particle Groups from $Al^{27}(d,\alpha)Mg^{25}$*

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The alpha-particle groups produced by the bombardment of aluminum by 10.8-Mev deuterons have been measured using nuclear emulsion plates for detection. Seven new levels in Mg^{25} were found at 6.98, 7.85, 8.62, 9.06, 975, 10.78, and 11.89 Mev. The previously known level at 4.01 Mev has been resolved into two levels at 3.96 and 4.12 Mev.

INTRODUCTION

SEVERAL investigations have been made of the lower-lying levels in Mg^{25} from the $Al^{27}(d,\alpha)Mg^{25}$ reaction.[1] Recently Schelberg, Sampson, and Cochran[2] extended this work to show ten levels in Mg^{25} with a maximum excitation of 6 Mev.

The present investigation was initiated with the aim of extending this work to higher excitations since the previous results showed an approximately constant level spacing of about 0.6 Mev. The energy levels above 7 Mev in Mg^{25} have been obtained in neutron scattering experiments,[3] and it seemed of interest to extend the $Al^{27}(d,\alpha)Mg^{25}$ work to overlap this region.

The present investigation was carried out with the use of nuclear emulsions as detectors to facilitate the measurement of lower energy alpha-particles leading to higher excitation in the residual nucleus. The results for lower energy alpha-particles were limited however, by the presence of background tracks.

EXPERIMENTAL PROCEDURE

The deuteron bombardments of the target were made in the same way as previously described.[2] The deuterons from the Indiana University cyclotron were passed through the analyzing magnet before striking the target foil. The beam energy was thus determined to be 10.82±0.08 Mev and was held at this value for the duration of the bombardment.

The targets were of aluminum foil, 0.17 mg/cm^2 surface density, and were supported by a brass ring in such a manner that the beam was prevented from striking the brass. Fresh targets were prepared for each bombardment to reduce the accumulation of contami-

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* This work was assisted by the joint program of the ONR and AEC.

[1] E. McMillan and E. O. Lawrence, Phys. Rev. **47**, 343 (1935); Pollard, Sailor, and Wyly, Phys. Rev. **75**, 725 (1949); A. P. French and P. B. Treacy, Proc. Phys. Soc. (London) **63**, 665 (1950).

[2] Schelberg, Sampson, and Cochran, Phys. Rev. **80**, 574 (1950).

[3] D. E. Alburger and E. M. Hafner, Revs. Modern Phys. **22**, 373 (1950).