Energy Exchange between HD (B\(^1\) \(\Sigma_u^+\), \(v'\), \(J'\)) and Ground State H\(_2\) and D\(_2\) by Interaction of Electronic Transition Dipole Moments

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Steady state fluorescence experiments with mixtures of HD and H\(_2\) or D\(_2\) have given effective cross sections for energy exchange processes in collisions of electronically excited HD and ground state H\(_2\) and D\(_2\) molecules in well defined quantum states. The experimental results are compared with first order calculations using the Sharma-Brau theory of energy transfer due to the interaction of transition dipole moments.

Introduction

Recently, Melton and Klemperer\(^1\) have shown that rapid exchange of electronic energy occurs in collisions of electronically excited 14NO (A\(^2\Sigma^+)\) and ground state 15NO molecules. They attributed the large energy exchange probabilities to the long range interaction of the transition dipole moments of the colliding molecules. Assuming this transition dipole potential, Gordon and Chiu\(^2\) have calculated the effective cross sections for these processes and have obtained excellent agreement with the experimental data. In both papers\(^1,2\) the authors point out that such energy exchange processes likewise could occur if the molecules are not distinguished by isotopic substitution, and then appear to be simply rotational and vibrational relaxation in the electronically excited state. Gordon and Chiu\(^2\) suggest that the extraordinarily efficient vibrational relaxation observed in electronically excited states\(^3,4\) might be explained by this type of process.

In previous work\(^5\) it has been shown that the near-resonant energy transfer from electronically excited argon atoms to H\(_2\), HD and D\(_2\) molecules\(^6\) can be explained likewise to a great extent by the dipole-dipole interaction. However, only relative cross sections could be measured, and a second type of energy transfer mechanism was observed which obviously contributed to many of the measured total cross sections.

In this paper we report on studies of energy exchange processes in collisions of electronically excited HD (B\(^1\) \(\Sigma_u^+\), \(v'\), \(J'\)) and ground state H\(_2\) or D\(_2\).

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molecules. Due to the large vibrational and rotational spacing of the H\(_2\), HD and D\(_2\) energy levels, absolute cross sections could be measured for a number of energy exchange processes (1),

\[
\text{HD} (B^1 \Sigma_u^+, v''', J''') + M_2 (X^2 \Sigma_g^+, v''''; J''''') \rightarrow \text{HD} (X^2 \Sigma_g^+, v''''; J'''''), M_2 (B^1 \Sigma_u^+, v'''; J'''') \pm \Delta E
\]

(M\(_2 = \text{H}_2 \text{ or D}_2\)) where the primary HD\(^*\) and M\(_2\) as well as the product molecules HD and M\(_2^*\) are in well defined quantum states. Such experimental data should be especially suited for a comparison with calculated cross sections.

HD molecules were selectively excited into three different vibrational and rotational levels of the B\(^1\) \(\Sigma_u^+\) state by absorption of the 1048 Å and 1066 Å argon resonance lines\(^7\). On the addition of H\(_2\) or D\(_2\) to the HD sample gas, the vacuum-uv fluorescence spectra besides the (B \(\rightarrow\) X) Lyman bands of HD also showed single lines of the Lyman bands of H\(_2\) and D\(_2\), respectively. Measurements of the pressure dependence of the relative intensities of the H\(_2\), HD and D\(_2\) fluorescence lines yielded effective cross sections for the energy exchange processes between HD\(^*\) and H\(_2\) or D\(_2\).

Calculations

Dipole-dipole interaction is known to yield large collision efficiencies only if the transitions involved are close to resonant\(^8\) to 12. Therefore we first calculated the energy discrepancies between all emission lines originating from the pumped levels of HD (B\(^1\) \(\Sigma_u^+\)) \((v' = 3, J' = 2; v' = 5, J' = 2; v' = 6, J' = 5\)) and absorption lines in the Lyman band systems of H\(_2\) and D\(_2\). The spectroscopic constants
Table 1. Near-resonant energy exchange processes between HD* and ground state hydrogen molecules.

<table>
<thead>
<tr>
<th>HD*($v_i', J_i'$) + M ($v_i'', J_i''$) → HD ($v_{i''}', J_{i''}'$) M* ($v_i', J_i$)</th>
<th>$\pm \Delta E$ (cm$^{-1}$)</th>
<th>$N_f'/\Sigma N_j'$</th>
<th>$\mu_{HD}^2 \mu_{H_2}^2$ (10$^{-28}$ Debye$^4$)</th>
<th>dd-theory $Q_{DD} N_f'/\Sigma N_j'$ for $b^* = 7.0$ Å (Å$^2$)</th>
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</table>

used for these calculations were the same as in previous work$^7,13$. From these data we selected the processes (1) which have energy defects $\Delta E$ of less than 100 cm$^{-1}$; some of them are shown in Table 1. It is seen that a large number of such processes should occur. HD transitions to levels $v'' = 0, J''$ and $v'' = 1, J''$ of the ground state are involved.

The calculation of collision cross sections for energy exchange processes due to the long range interaction of electric multipole moments is performed using an equation for the collision probability $P(b, v)$ which was first derived by Van Kranendonk$^8$ for line broadening problems. He used a semiclassical method based on time-dependent perturbation theory and straight line constant velocity trajectories. The same result was later obtained by quantum mechanical calculations of Cross and Gordon$^9$ who used the first Born approximation. The theory was first applied to calculate cross sections for energy exchange processes due to the interaction of transition multipole moments by Mahan$^{10}$ and Sharma and Braun$^{11}$. According to Eq. (8) of Ref. 11 the probability for energy exchange between HD* and H$_2$ is given by Equation (2).

$$P(b, v) = \frac{8 \mu_{HD}^2 \mu_{H_2}^2}{9 \hbar^2 v^2 b^4} C_{HD}^2 (J_1' 1 J_1'' | 00) \cdot C_{H_2}^2 (J'' | 00) R(x) ,$$

(2)

$$R(x) = (1 + 2x + (3/4)x^2 + \pi x^3) \exp \{-2x\} .$$

Here $x = |\Delta E|/b/h v$, $b$ is the impact parameter, $v$ the relative velocity, $\mu_{HD}^2$ and $\mu_{H_2}^2$ are the squares of the transition dipole moments of the HD and H$_2$ bands involved. The Clebsch-Gordan coefficients $C_{HD}^2 (J_1' 1 J_1'' | 00)$ are the rotational parts of the line oscillator strengths, and are calculated from the Hön-London formula$^{14}$ and the statistical weights of the rotational levels. The squares of the dipole moments were calculated from the transition probabilities given by Allison and Dalgarno$^{15}$ according to Equation (3).

$$\mu^2_{v'v''} = \frac{3 \hbar^2 \beta_{v'v''}^2 A_{v'v''}}{32 \pi^3} .$$

(3)

Using Eq. (2) for the calculation of cross sections, brings up the problem of how to treat the close
collisions in which the impact parameter $b$ is smaller than the hard sphere radius $d$, and for which the straight line approximation cannot be valid. It is seen that the probability given by Eq. (2) exceeds unity if $b \rightarrow 0$. We have performed the calculations as in the previous work on electronic energy exchange between argon and hydrogen. The cross section is obtained by numerical integration of $P(b,v)$ over impact parameter and averaging over the Maxwell-Boltzmann velocity distribution. $P(b,v)$ is set equal to zero unless there is enough initial kinetic energy for the collisionally induced transition to occur. If the transition can occur, $v$ is taken as the average of the velocities in the initial and the final states. To account for the breakdown of Eq. (2) in close collisions a parameter $b^*$ is introduced which represents some average distance of closest approach for which the assumption of a straight line trajectory is valid, and $P(b,v) = P(b^*,v)$ is used for $0 \leq b \leq b^*$. Finally, $P(b,v)$ is arbitrarily limited at the value of 0.5. However, for the transitions considered here, a probability greater than 0.5 was not predicted for any significant values of the variables $b$ and $v$. Hence, this “chopping off” of the probability was not an important feature of the calculations.

The cross sections were also calculated by using Sharma's equation for the velocity averaged energy exchange probability [Eq. (33) of Ref. 12]. Here the main difference is that in deriving this equation the collision probability for impact parameters $0 \leq b \leq b^*$ was estimated by interpolating between $P(0,v)$ and $P(b^*,v)$ with the parabola

$$P(b,v) = P(0,v) + (b^2/b^*2)[P(b^*,v) - P(0,v)] .$$

As was expected, for equal values of $b^*$ these calculations yielded cross sections which were up to 30% smaller than those obtained by the first computation method.

An even simpler method for calculating the dipole-dipole cross sections was suggested by Gordon and Chiu and was applied to calculate cross sections for energy exchange in NO*–NO collisions. Using this method we obtained cross sections which in most cases were much larger than those obtained by the other calculations. Especially for large values of $\Delta E$ ($\Delta E = 50 - 100 \text{ cm}^{-1}$) this discrepancy increased up to two orders of magnitude. In all cases the limiting $b^*$ values, defined by

$$P(b^*,v) = E_f/(E_i + E_f),$$

where $E_i$ and $E_f$ are the initial and final translational energies, down to which in this method the probability function (2) is used, were less than 4 Å, the estimated hard sphere radius of HD*–H$_2$ collisions. Thus the function (2) is used in regions of impact parameter where the assumptions of the theory are certainly not valid. Obviously, this simplified computation method can be used only in cases where the transition dipole moments are large and $\Delta E$ is small, such that the limiting $b$ value is greater than the hard sphere radius $d$.

Since the rotational levels $J''$ of the ground state H$_2$ and D$_2$ molecules are not equally populated at room temperature, the quantities which determine the occurrence of the processes, are the products of the collision cross section $Q$ and the relative population density in the initial state $J''$, $Q \cdot N_{J''}/\Sigma_{J''} N_{J''}$. These data were calculated with the cross sections obtained by the first computation method for $b^* = 7$ Å. The results are shown in the last column of Table 1.

### Experiments

The fluorescence measurements were made using an argon lamp, fluorescence cell and gas handling system similar to that described previously. The monochromator was a 1 meter instrument (Hilger and Watts, type E 766), equipped with a 1200 lines/mm grating blazed for 1200 Å, which, with the slits set at 40 μm width and 10 mm height each, yielded a line half width of 0.4 Å. A Bendix BX 762 channeltron photomultiplier with CsI photocathode was used which had a dark counting rate of less than 0.5 counts/s. The gases He, Ar, H$_2$, and D$_2$ were research grade containing less than 5 ppm impurities. The HD from Merck was used without further purification.

Details of the excitation processes are given in Reference 7. Figure 1 shows fluorescence spectra which were measured for different compositions of the sample gas in the wavelength region between 1605 and 1615 Å. The fourth trace from the bottom shows that with a mixture of HD and H$_2$ several lines at 1607.9, 1610.3 and 1613.2 Å are observed which are not present in the spectrum of pure HD nor in that of pure H$_2$. These lines are easily identified to be the R(1), P(1) and P(3) lines of the (5,12) band in the Lyman system of H$_2$. The H$_2^*$ ($v' = 5, J' = 0$ and 2) levels from which these lines originate, belong to those H$_2$ states which are...
expected to be populated in collisions of ground state H₂ with HD\(^*\) (\(v' = 6, J' = 5\)) molecules (Table 1). Strong R(4) and P(6) lines from this pumped HD\(^*\) level are observed at 1606.0 and 1614.2 Å. The upper trace in Fig. 1 shows the effect of He added to the same total pressure. It is seen that He causes much stronger rotational relaxation within the \(v' = 6\) level of HD\(^*\) than does H₂.

In order to determine the cross sections for the observed energy exchange processes, the intensities of lines from, for instance, the (\(v' = 5, J' = 0\)) level of H₂\(^*\) and the (\(v' = 6, J' = 5\)) level of HD\(^*\) were measured as a function of H₂ pressure. From the line intensities the population ratios were calculated in the usual way by dividing the intensities by the line transition probabilities \(A_{v'v''}^J\) which were calculated from the band transition probabilities \(A_{v'v''}^k\) and the rotational line strengths. A steady state treatment of the system leads to the simple Eq. (5),

\[
\frac{N_{\text{HD}^*}}{N_{\text{H}_2^*}} = \frac{1}{k_{\text{HD}^*-\text{H}_2}} \frac{1}{N_{\text{H}_2}} - \frac{k_{\text{H}_2^*}}{k_{\text{HD}^*-\text{H}_2}},
\]  

(5)

where \(N_{\text{HD}^*}\), \(N_{\text{H}_2^*}\), and \(N_{\text{H}_2}\) are the concentrations of the HD\(^*\), H₂\(^*\), and H₂ molecules in the specific vibrational and rotational states involved, \(k = k/k_{\text{HS}^*}\) is the rate constant for the total radiative decay of the H₂\(^*\) level, \(k_{\text{HD}^*-\text{H}_2}\) is the bimolecular rate constant for the energy exchange process from HD\(^*\) to H₂, and \(k_{\text{HS}^*}\) is the sum of the rate constants for all collisional processes (rotational relaxation, vibrational relaxation and quenching) depleting the excited H₂\(^*\) molecules. According to Eq. (5), if the ratio of the concentrations in the pumped HD\(^*\) level and in the collisionally populated H₂\(^*\) level is plotted as a function of reciprocal H₂ pressure, a straight line should be obtained. Figure 2 shows such a plot. Whenever it was possible, measurements in different HD and H₂ bands were performed to ensure that no accidental superposition of unknown lines influenced the data. For instance, in Fig. 1 one could argue that the line observed at 1610.3 Å was the P(3) line of the HD (6,14) band, which is nearly at the same wavelength as the H₂ line, and that the HD\(^*\) (\(v' = 6, J' = 2\)) level might be preferably populated by a near resonant rotational
energy transfer process. However, if any, then the 
\((v' = 6, J' = 1)\) level should be populated by such a 
process, which, however, is not observed. The energy 
step from \(J = 5\) to \(J = 1\) is 324 cm\(^{-1}\) and is close 
to that from \(J'' = 0\) to \(J'' = 2\) in the ground state of 
\(H_2\), which is 354 cm\(^{-1}\).

From the slopes of the curves like that in Fig. 2, 
the rate constants of the energy exchange processes 
were determined. The intercepts of the lines yielded 
rough data for \(k_{M^*}\), the sum of the rate constants 
of all collisional processes deactivating the \(M^*\) 
levels. Effective cross sections were obtained in the 
usual way by dividing the rate constants by the 
relative velocity of the colliding molecules. The 
ergy transfer cross sections for the processes 
which have been studied hitherto are collected in 
Table 2. The total deactivation occurs with cross 
sections between 20 and 80 Å\(^2\).

**Discussion**

The hard sphere radius \(d_{\text{HD}^*-\text{H}_2}\) of the \(\text{HD}^*-\text{H}_2\) 
collisions may be estimated by (6),

\[
d_{\text{HD}^*-\text{H}_2} \approx \frac{1}{2} \left( d_{\text{HD}^*-\text{H}_2^*} \left( 1 + \frac{r_e}{r_e} \right) \right),
\]

where \(d_{\text{HD}^*-\text{H}_2}\) is the hard sphere radius for colli­
sions of the ground state molecules, and \(r_e^*\) and \(r_e\) 
are the equilibrium internuclear distances in the 
\(B^1\Sigma_u^+\) and \(X^1\Sigma_g^+\) states, respectively. This estima­
tion leads to \(d_{\text{HD}^*-\text{H}_2} \approx 4\) Å.\(^{13,18}\) In comparing the 
experimental results with the theoretical data ob­
tained by the first computation method, it is found 
that for \(b^* = 4\) Å, the calculated cross sections are 
by a factor of 2 to 6 larger than the experimental 
results (Table 2). Good agreement between the ex­
perimental and the calculated data is obtained for 
\(b^* = 7.0\) Å, which is, however, a rather unlikely high 
value for \(d_{\text{HD}^*-\text{H}_2}.\)\(^{19}\) The large discrepancy 
between the experimental and theoretical results for 
\(b^* = 4\) Å most likely is due to the efficient quenching 
of \(\text{HD}^*\) competing with the energy exchange proces­
ses in \(\text{HD}^*-\text{H}_2\) collisions. The effective cross sections 
for quenching are by a factor of 10 to 20 
larger than those for energy exchange.\(^7\) Therefore 
most of the collisions which in the absence of 
quenching would have led to energy exchange actu­
ally will result in quenching. Thus the yield to 
energy exchange is strongly reduced. The same effect 
was observed by Steinfeld and Schweid\(^{20}\) in studies 
of vibrational energy transfer in electronically ex­
cited iodine.

The cross sections for total deactivation are in 
the same order of magnitude as the cross section for 
self-quenching of \(\text{HD}^*\) by \(\text{HD}^*\) measured previ­
ously, and probably are mostly due to quenching.\(^7\)\(^\text{21}\) 
Further studies of the quenching processes and mea­
surements of the temperature dependence of the 
energy exchange cross sections are under way to get 
a better understanding of the \(\text{HD}^*-\text{H}_2\) collisions.

It is interesting to note that the value of \(b^*\) for 
which most of the theoretical data are in very good 
agreement with the experimental results (\(b^* = 7.0\) Å), 
is nearly equal to that which was found to repro­
duce most satisfactorily the relative cross sections 
of electronic energy transfer from argon to hydro­
gen \(^b\) \((b^* = 6.5 \pm 1.0\) Å\). This suggests that in this 
case similar effective quenching collisions compete 
with the energy exchange processes, too. This could

**Table 2. Effective cross sections of energy exchange processes**

<table>
<thead>
<tr>
<th>(M_2)</th>
<th>(v'i', J'i')</th>
<th>(v''i', J''i')</th>
<th>(v'i', J'i')</th>
<th>(v''i', J''i')</th>
<th>(\Delta E (\text{cm}^{-1}))</th>
<th>(Q_{dd} N_{j'}/\sum N_{j'i'} (\text{Å}^2))</th>
<th>(\text{dd-Theory, } b^* (\text{Å}))</th>
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<td>6.5</td>
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<td>0.4</td>
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\(^a\) Computed according to Eq. (33) of Ref. \(^{12}\).

\(^b\) Calculated by numerical integration of Eq. (2) over \(b\) and \(v\).
be established by measuring the yield of H atoms which are probably produced in the quenching process.


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