Energy Exchange between HD $(B^1\sum_u^+, v', J')$ 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 $^{14}NO(A^2\Sigma^+)$ and ground state ^{15}NO 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 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),

$$\begin{aligned} &HD(B^1\Sigma_u^+, v_i', J_i') + M_2(X^1\Sigma_g^+, v_i'', J_i'') \qquad (1)\\ &\rightarrow HD(X^1\Sigma_g^+, v_f'', J_f'') + M_2(B^1\Sigma_u^+, v_f', J_f') \pm \Delta E \end{aligned}$$

($M_2 = H_2$ 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[8–12]. 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

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Table 1. Near-resonant energy exchange processes between HD* and ground state hydrogen molecules.

HD*(v_i', J_i')	$+ M_2(v_i'', J_i'')$	→ HD(v_f'', J_f'')	$M_2^*(v_f', J_f')$	$\pm\Delta E$ (cm^{-1})	$N_{J_i''}/\Sigma N_{J_i''}$	$\mu^2_{HD}\,\mu^2_{M_2}$ (10^{-2} Debye^4)	dd-theory $Q_{dd}\,N_{J_i''}/\Sigma N_{J_i''}$ for $b^* = 7.0$ Å (Å^2)
3,2	H_2 0,3	0,1	3,4	68.1	0.090	0.521	0.034
3,2	0,1	1,1	0,0	33.3	0.658	0.058	0.27
3,2	0,2	1,1	0,3	38.0	0.117	0.199	0.069
5,2	0,3	0,1	5,2	19.8	0.090	0.757	0.61
5,2	0,4	0,3	5,3	−53.0	0.004	1.881	0.009
5,2	0,3	1,1	2,2	19.4	0.090	0.532	0.43
6,5	0,1	0,4	5,0	23.0	0.658	0.625	3.67
6,5	0,1	0,4	5,2	−70.5	0.658	2.490	0.66
6,5	0,1	1,4	2,2	−37.1	0.658	1.257	1.91
3,2	HD 0,5	0,1	4,4	− 9.7	0.0038	0.337	0.018
3,2	0,0	0,1	3,1	−37.5	0.200	1.023	0.35
3,2	0,3	1,1	0,4	−39.1	0.107	0.079	0.024
5,2	0,0	0,1	5,1	−40.8	0.200	3.170	0.90
5,2	0,1	0,1	5,0	72.7	0.389	0.354	0.11
5,2	0,3	1,1	2,2	8.4	0.107	0.307	0.52
6,5	0,3	0,4	6,2	−73.8	0.107	0.922	0.041
6,5	0,4	0,6	5,5	56.6	0.025	2.210	0.047
6,5	0,0	1,4	2,1	60.3	0.200	1.650	0.15
3,2	D_2 0,5	0,1	4,6	−13.5	0.015	0.223	0.041
3,2	0,2	0,3	3,3	−27.1	0.423	0.401	0.60
3,2	0,6	0,3	4,5	− 7.9	0.0068	0.393	0.031
5,2	0,2	0,1	6,1	0.5	0.423	0.382	3.08
5,2	0,3	0,1	6,4	36.0	0.125	0.778	0.34
5,2	0,6	0,1	7,5	4.1	0.0068	0.612	0.073
6,5	0,4	0,4	7,3	− 2.5	0.103	0.773	1.28
6,5	0,7	0,4	8,6	− 0.3	0.0006	0.967	0.008
6,5	0,5	0,4	7,6	61.5	0.015	1.169	0.013

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 ΔE 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 base 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 Brau [11]. According to Eq. (8) of Ref. 11 the probability for energy exchange between HD* and H_2 is given by Equation (2).

$$P(b, v) = \frac{8\,\mu^2_{HD}\,\mu^2_{H_2}}{9\,\hbar^2\,v^2\,b^4}\,C^2_{HD}\,(J_i'\,1\,J_f''\,|\,00) \cdot C^2_{H_2}\,(J_i''\,1\,J_f'\,|\,00)\,R(x)\,, \qquad (2)$$

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

Here $x = |\Delta E|\,b/\hbar\,v$, b is the impact parameter, v the relative velocity, $\mu^2_{HD}$and $\mu^2_{H_2}$ are the squares of the transition dipole moments of the HD and H_2 bands involved. The Clebsch-Gordan coefficients $C^2(J_i\,1\,J_f\,|\,00)$ are the rotational parts of the line oscillator strengths, and are calculated from the Hönl-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).

$$\mu^2_{v'v''} = \frac{3\,\hbar\,\lambda^3_{v'v''}\,A_{v'v''}}{32\,\pi^3}\,. \qquad (3)$$

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[5]. 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 $0 \leqq b \leqq b^*$. Finally, $P(b, v)$ is arbitrarily limited at the value of 0.5[16]. 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 $0 \leqq b \leqq b^*$ was estimated by interpolating between $P(0, v)$ and $P(b^*, v)$ with the parabola[11, 12]

$$P(b, v) = P(0, v) + (b^2/b^{*2})\,[P(b^*, v) - P(0, v)]\,. \qquad (4)$$

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[2] and was applied to calculate cross sections for energy exchange in $NO^* - NO$ collisions[2, 17]. 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 ΔE ($\Delta E = 50 - 100\ \mathrm{cm}^{-1}$) this discrepancy increased up to two orders of magnitude. In all cases the limiting b^* values, defined by $P(b^*, \bar{v}) = E_f/(E_i + E_f)$, 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 ΔE is small, such that the limiting b value is greater than the hard sphere radius d.

Since the rotational levels J_i'' 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_i'', $Q \cdot N_{J_i''}/\Sigma_{J_i''} N_{J_i''}$. 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

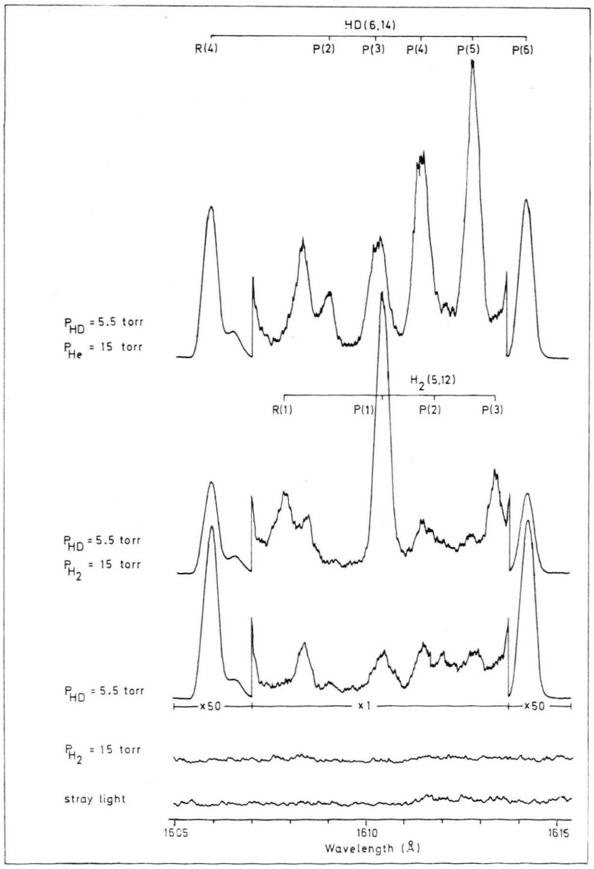
The fluorescence measurements were made using an argon lamp, fluorescence cell and gas handling system similar to that described previously[7]. The monochromator was a 1 meter instrument (Hilger and Watts, type E 766), equipped with a 1200 lines/mm grating blazed for 1200 Å, which, with the slits set 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 H_2 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 H_2.

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 H_2^* and the $(v'=6, J'=5)$ level of HD* were measured as a function of H_2 pressure. From the line intensities the population ratios were calculated in the usual way by dividing the intensities by the line transition probabilities $A_{v'J'v''J''}$ which were calculated from the band transition probabilities $A_{v'v''}$ [15] and the rotational line strengths [14]. A steady state treatment of the system leads to the simple Eq. (5),

$$\frac{N_{\mathrm{HD}^*}}{N_{\mathrm{H}_2^*}} = \frac{1}{\tilde{k}_{\mathrm{HD}^*-\mathrm{H}_2}} \frac{1}{N_{\mathrm{H}_2}} - \frac{\tilde{k}^{t}_{\mathrm{H}_2^*}}{\tilde{k}_{\mathrm{HD}^*-\mathrm{H}_2}}, \qquad (5)$$

where N_{HD^*}, $N_{\mathrm{H}_2^*}$, and N_{H_2} are the concentrations of the HD*, H_2*, and H_2 molecules in the specific vibrational and rotational states involved, $\tilde{k} = k/k^{s}_{\mathrm{H}_2^*}$ where $k^{s}_{\mathrm{H}_2^*}$ is the rate constant for the total radiative decay of the H_2* level, $k_{\mathrm{HD}^*-\mathrm{H}_2}$ is the bimolecular rate constant for the energy exchange process from HD* to H_2, and $k^{t}_{\mathrm{H}_2^*}$ is the sum of the rate constants for all collisional processes (rotational relaxation, vibrational relaxation and quenching) depleting the excited H_2* molecules. According to Eq. (5), if the ratio of the concentrations in the pumped HD* level and in the collisionally populated H_2* level is plotted as a function of reciprocal H_2 pressure, a straight line should be obtained. Figure 2 shows such a plot. Whenever it was possible, measurements in different HD and H_2 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 H_2 line, and that the HD* $(v'=6, J'=2)$ level might be preferably populated by a near resonant rotational



← Fig. 1. Fluorescence spectra in the wavelength region from 1605 to 1615 Å from different mixtures of sample gas.

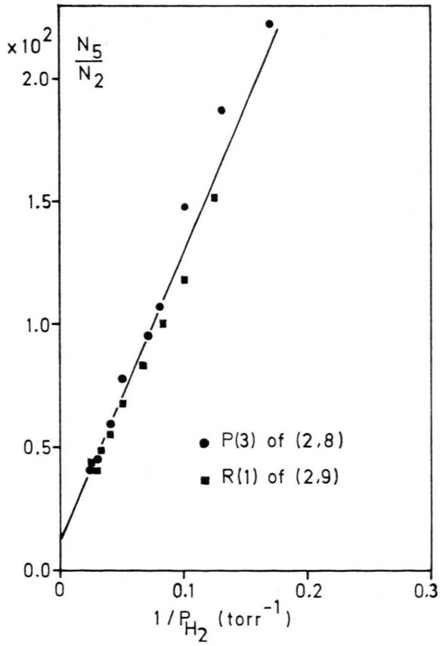


Fig. 2. Population ratio N_5/N_2 of HD* $(v'=6, J'=5)$ and H_2* $(v'=2, J'=2)$ levels as a function of reciprocal H_2 pressure. The weak H_2 lines were measured in the (2,8) and (2,9) bands. The strong P(6) line of the HD(6,14) band (Fig. 1) was used to monitor HD* $(v'=6, J'=5)$.

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 $k^{t}_{M_2^*}$, the sum of the rate constants of all collisional processes deactivating the M_2^* levels. Effective cross sections were obtained in the usual way by dividing the rate constants by the relative velocity of the colliding molecules. The energy exchange 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 $d_{HD^*-H_2}$ of the HD^*-H_2 collisions may be estimated by (6),

$$d_{HD^*-H_2} \cong \tfrac{1}{2}\, d_{HD-H_2} \cdot (1 + (r_e^*/r_e))\,, \qquad (6)$$

where d_{HD-H_2} is the hard sphere radius for collisions 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 estimation leads to $d_{HD^*-H_2} \cong 4$ Å [13, 18]. In comparing the experimental results with the theoretical data obtained 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 experimental and the calculated data is obtained for $b^* = 7.0$ Å, which is, however, a rather unlikely high value for $d_{HD^*-H_2}$ [19]. The large discrepancy between the experimental and theoretical results for $b^* = 4$ Å most likely is due to the efficient quenching of HD* competing with the energy exchange processes in HD^*-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 actually 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 excited iodine.

The cross sections for total deactivation are in the same order of magnitude as the cross section for self-quenching of HD* by HD [7] measured previously, and probably are mostly due to quenching [7, 21]. Further studies of the quenching processes and measurements of the temperature dependence of the energy exchange cross sections are under way to get a better understanding of the HD^*-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 reproduce most satisfactorily the relative cross sections of electronic energy transfer from argon to hydrogen [5] ($b^* = 6.5 \pm 1.0$ 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

$$HD^*(v_i', J_i') + M_2(v_i'', J_i'') \rightarrow HD(v_f'', J_f'') + M_2^*(v_f', J_f') \pm \Delta E\,.$$

						$Q_{dd}\, N_{J_i''}/\Sigma N_{J_i''}$ (Å^2)						
M_2	$v_i'\, J_i'$	v_i'', J_i''	v_f'', J_f''	v_f', J_f'	ΔE (cm^{-1})	Experiment	dd-Theory, b^* (Å)					
							4.0 [a]	4.0 [b]	6.0 [b]	6.5 [b]	7.0 [b]	7.5 [b]
D_2	6,5	0,4	0,4	7,3	− 2.5	1.8 ± 0.8	3.9	3.2	1.8	1.5	1.3	1.1
H_2	6,5	0,1	0,4	5,0	23.0	3.6 ± 0.4	13.3	15.0	5.7	4.6	3.7	3.0
D_2	3,2	0,2	0,3	3,3	−27.1	0.69 ± 0.15	2.7	3.6	1.0	0.78	0.60	0.46
H_2	3,2	0,1	1,1	0,0	33.3	0.28 ± 0.06	1.20	1.5	0.45	0.34	0.27	0.21
H_2	6,5	0,1	1,4	2,2	−37.1	1.7 ± 0.3	9.9	12.8	3.4	2.5	1.9	1.4
H_2	6,5	0,1	0,4	5,2	−70.5	1.7 ± 0.3	8.6	9.7	1.5	0.99	0.66	0.44

[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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