

## $H^{79}Br$ 과 $H^{81}Br$ 간의 진동→진동에너지 이동

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## Vibration-Vibration Energy Transfer between $H^{79}Br$ and $H^{81}Br$

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**요약.** 공명 진동→진동 에너지 이동 과정,  $H^{79}Br(v=1) + H^{81}Br(v=0) \rightarrow H^{79}Br(v=0) + H^{81}Br(v=1) + \Delta E = 0.38 \text{ cm}^{-1}$ 에 대해 long-lived 충돌모형을 적용하여 에너지 이동 확률을 200-800 K 범위에서 계산하였다. 계산된 확률은 온도가 상승함에 따라 감소하며 온도 의존성은  $P \propto T^{-1.8}$  이었다. 또한 계산된 확률은 다른 이론들로부터 계산한 확률들 보다 알려져 있는 실험치와 더 잘 일치하였다.

**ABSTRACT.** The long-lived collision model has been applied to the resonant vibration-vibration energy exchange process  $H^{79}Br(v=1) + H^{81}Br(v=0) \rightarrow H^{79}Br(v=0) + H^{81}Br(v=1) + \Delta E = 0.38 \text{ cm}^{-1}$ . The energy exchange probabilities have been calculated over the temperature range from 200 to 800 K. They show negative temperature dependence ( $P \propto T^{-1.8}$ ) and agree with the available experimental data better than those calculated from other theories.

### 1. INTRODUCTION

In recent years there has been much interest directed towards the vibration-to-vibration ( $V \rightarrow V$ ) energy exchange processes between the hydrogen halide molecules differing only by isotopic substitutions<sup>1-6</sup>. The reasons why these processes have attracted many workers are as follows. First, they have practical application in isotope separation schemes using chemical lasers<sup>7-10</sup>. Second, these  $V \rightarrow V$  energy exchange rates are needed to model accurately chemical lasers and to understand their operational mechanism<sup>11</sup>. Finally, and perhaps of most importance, the experimental measurements provide the theorists with an opportunity to

test various theories used to predict these  $V \rightarrow V$  energy exchange probabilities.<sup>2</sup>

Recently, Horwitz and Leone measured the  $V \rightarrow V$  energy exchange probability for the following process and obtained  $P=0.098$  at 298 K<sup>2</sup>:  $H^{79}Br(v=1) + H^{81}Br(v=0) \rightarrow H^{79}Br(v=0) + H^{81}Br(v=1) + \Delta E = 0.38 \text{ cm}^{-1}$ . Since the energy mismatch  $\Delta E$  is almost equal to zero, this process is an ideal case for testing various resonant  $V \rightarrow V$  energy exchange theories and determining what kind of feature in the intermolecular interaction potential plays the most important role in bringing about the  $V \rightarrow V$  energy exchange.

In a series of papers Shin recognized the importance of the strong hydrogen bond energy

and developed a collision model which considers restricted translational motion of the colliding partners as the relevant local mode to the near resonant  $V \rightarrow V$  energy exchange between the hydrogen fluoride molecules<sup>12-14</sup>. This so-called loosely-held, non-rigid dimer collision model has recently been modified to take into account the relatively weak hydrogen bonding between the hydrogen chloride molecules and this modified version has been shown to be very satisfactory in explaining the  $V \rightarrow V$  energy exchange between  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  molecules<sup>4</sup>.

In this paper we shall apply this theory to  $\text{H}^{79}\text{Br} (v=1) + \text{H}^{81}\text{Br} (v=0) \rightarrow \text{H}^{79}\text{Br} (v=0) + \text{H}^{81}\text{Br} (v=1) + \Delta E$  process and determine the temperature dependence of the  $V \rightarrow V$  energy exchange probability. Also, the results will be compared with those calculated from other resonant  $V \rightarrow V$  energy transfer theories.

## 2. COLLISION MODEL AND ENERGY EXCHANGE PROBABILITY

Since the description of the collision model and the derivation of the  $V \rightarrow V$  energy exchange probability are given in Ref. 4, we give here only those expressions that are essential for calculation.

The intermolecular interaction potential is assumed to be of Morse type which contains both the short-range repulsive and the long-range attractive parts,

$$U(r) = D \{ \exp \{ (r_e - r)/a \} - 2 \exp \{ (r_e - r)/2a \} \} \quad (1)$$

where  $r$  is the distance between Br of one molecule and H of the other molecule,  $r_e$  its equilibrium value,  $a$  the usual potential range parameter, and  $D$  the depth of the potential well representing the contribution of strong molecular attraction.

Then the perturbation energy which causes

$V \rightarrow V$  energy exchange after including the effect rotational motion of molecules can be expressed as

$$V[R(t), \theta_1, \theta_2, \chi_1, \chi_2] = \{ (2\pi)^{-2} \int_0^{2\pi} \int_0^{2\pi} F(t, \theta_1, \theta_2) d\theta_1 d\theta_2 \} \mathbf{a}_1 \mathbf{a}_2^+ \quad (2)$$

where  $R$  is the distance between the centers of mass of the two molecules,  $\theta$  the angle between the molecular axis and the vector  $R$ ,  $\chi$  the vibrational amplitude,  $\mathbf{a}$  and  $\mathbf{a}^+$  are the usual ladder operators<sup>15</sup>. The subscripts 1 and 2 refer to  $\text{H}^{79}\text{Br}$  and  $\text{H}^{81}\text{Br}$  molecule, respectively. The quantity  $F$  in Eq. (2) is given by

$$F = \left( \frac{\hbar}{2M_1\omega_1} \right)^{1/2} \left( \frac{\hbar}{2M_2\omega_2} \right)^{1/2} D \gamma_1 \gamma_2 a^{-2} \left\{ \exp \{ (r_e - r)/a \} \exp \{ -Q_1 (\cos\theta_{1e} - \cos\theta_1) \} \right. \\ \times \left[ \exp \{ Q_2 (\cos\theta_{2e} - \cos\theta_2) \} - \frac{1}{2} \exp \{ (r_e - r)/2a \} \exp \{ -\frac{1}{2} Q_1 (\cos\theta_{1e} - \cos\theta_1) \} \right. \\ \left. \left. \times \left[ \exp \{ \frac{1}{2} Q_2 (\cos\theta_{2e} - \cos\theta_2) \} \right] \cos\theta_1 \cos\theta_2 \right] \right\} \quad (3)$$

where  $M$  and  $\omega$  are the reduced mass and angular frequency, respectively;  $\gamma_1$  and  $\gamma_2$  are mass ratios defined as  $\gamma_1 = m_{\text{Br}^{79}}/m_{\text{H}^{79}\text{Br}}$  and  $\gamma_2 = m_{\text{Br}^{81}}/m_{\text{H}^{81}\text{Br}}$ . The dimensionless parameters  $Q_1$  and  $Q_2$  are defined as  $Q_1 = \gamma_1 d_1/a$  and  $Q_2 = \gamma_2 d_2/a$ . Here  $d$  is the equilibrium bond distance of  $\text{HBr}$ .

The  $10 \rightarrow 01$   $V \rightarrow V$  transition probability obtained from the perturbed wave equation is<sup>16</sup>

$$P_{10}^{01}(E) = \frac{\sin^2 W}{1 + q^2} \quad (4)$$

where  $E$  is the collision energy,  $W = (1 + q^2)^{1/2} \hbar^{-1} \int \bar{F}(t) dt$ ,  $\bar{F}(t)$  the angle averaged quantity in the square bracket of Eq. (2),  $q = \Delta E/2G$ , and  $G = \tau^{-1} \int \bar{F}(t) dt$ ,  $\tau$  being the duration of collision.

Finally the thermal probability after consider-

ing collisions with non-zero impact parameter becomes

$$P_{10}^0(T) = \frac{1}{(kT)^2 \pi R^{*2}} \int_0^{R^*} \int_0^{D^*} 2\pi b E P_{10}^0(E, b) dE db \quad (5)$$

where  $R^*$  is the hard-sphere collision diameter,  $D^*$  modified hydrogen bond energy due to orientation averaging, and  $b$  the impact parameter.

### 3. CALCULATION

The molecular parameters required for calculation are  $\omega$  and  $d$ . For H<sup>79</sup>Br we take  $\omega_e = 2649.67 \text{ cm}^{-1}$  and  $\omega_e x_e = 45.21 \text{ cm}^{-1}$ .<sup>17</sup> Then  $\omega$  for H<sup>79</sup>Br becomes  $\omega = \omega_e - 2\omega_e x_e = 2559.25 \text{ cm}^{-1}$ , and that for H<sup>81</sup>Br is  $2559.25 - 0.38 = 2558.87 \text{ cm}^{-1}$ . For the equilibrium interatomic distance  $d$ , we take  $1.414 \text{ \AA}$  for both molecules<sup>17</sup>.

In addition to these we also need collisional parameters  $a$ ,  $D$ , and  $R^*$ . The range parameter  $a$  is usually in the range of  $0.2 - 0.3 \text{ \AA}$ .<sup>1, 8-20</sup> Since  $a = 0.25 \text{ \AA}$  gave the most satisfactory results in the case of H<sup>35</sup>Cl + H<sup>37</sup>Cl system, we use the same value in this study too. The hydrogen bond energy for HBr is not known. However, from the similarities in the heats of vaporization of HCl and HBr, we may assume that HBr and HCl have about the same hydrogen bond energy<sup>21</sup>. Since the hydrogen bond energy for HCl is  $2.1 \text{ kcal/mol}$ <sup>22</sup>, we take  $2.0 \text{ kcal/mol}$  as that for HBr. The hard sphere collision diameter  $R^*$  is estimated to be between  $3.4 - 3.5 \text{ \AA}$ <sup>23, 24</sup> and we shall take  $3.5 \text{ \AA}$ . The integration in eq. (4) was performed numerically, and the calculation of the  $V \rightarrow V$  energy exchange probabilities was carried out for the temperature range from 200 to 800 K where the long-lived collision theory is expected to be valid.

### 4. RESULTS AND DISCUSSION

The  $V \rightarrow V$  energy exchange probabilities obtained theoretically in this work are shown as the solid curve in Fig. 1. First, the probability at 300 K is 0.06 and this compares very favorably with the experimental value 0.098. The calculated probabilities are not very sensitive to the change in either  $a$  or  $D$ . The variation of  $a$  from  $0.22$  to  $0.28 \text{ \AA}$  with  $D$  fixed at  $2.0 \text{ kcal/mol}$  causes the calculated probability change from  $0.04$  to  $0.08$ , and the change in the calculated probability corresponding to the variation of  $D$  from  $1.7$  to  $2.3 \text{ kcal/mol}$  with  $a$  fixed at  $2.5 \text{ \AA}$  ranges from  $0.05$  to  $0.07$ . Second, the calculated probabilities decrease with increasing temperature, *i.e.*, they exhibit

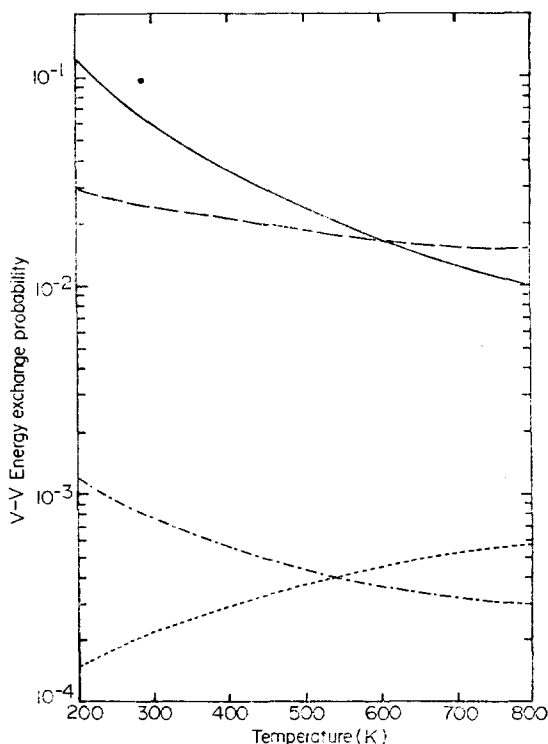


Fig. 1.  $V \rightarrow V$  Energy Exchange Probability for  $\text{H}^{79}\text{Br}(v=1) + \text{H}^{81}\text{Br}(v=0) \rightarrow \text{H}^{79}\text{Br}(v=0) + \text{H}^{81}\text{Br}(v=1)$ : — this work, - -  $P_M$ , - · -  $P_{SB}$ , ···  $P_{rep}$ , ○ exp. point from Ref. 2.

the so-called negative temperature dependence. The scarcity of the experimental data precludes an unequivocal verification of this trend. However, this behavior is typical, at least at low temperature, of the systems such as hydrogen fluorides<sup>6,12~14</sup> and hydrogen chlorides<sup>4</sup> in which the long-range attractive force plays a vital role, and we think this is true for HBr too. Third, the  $\ln P$  vs.  $\ln T$  plot gives a straight line with a slope of  $-1.8$  over the temperature range  $200 \sim 800$  K. This slope is nearly the same as that found experimentally<sup>3</sup>,  $-1.6$ , for the very similar process  $\text{H}^{35}\text{Cl}(v=1) + \text{H}^{37}\text{Cl}(v=0) \rightarrow \text{H}^{35}\text{Cl}(v=0) + \text{H}^{37}\text{Cl}(v=1)$ .

There are other theories which can be applied to the resonant  $V \rightarrow V$  energy exchange processes. In one theory only the experimentally repulsive part of the intermolecular potential is taken into consideration<sup>25</sup>. In this theory, the resonant  $V \rightarrow V$  energy exchange probability is given by the following equation<sup>26</sup>,

$$P = \frac{m_{\text{H}} m_{81\text{Br}}}{m_{\text{H}^{79}\text{Br}} m_{\text{H}^{81}\text{Br}} m_{\text{H}} m_{79\text{Br}}} \frac{2\mu kT}{\omega_1 \omega_2 a^2} \quad (6)$$

where  $\mu$  is the reduced mass of the collision system. The probabilities calculated using this equation is shown in Fig. 1 as the dotted line ( $P_{\text{rep}}$ ). The probability at 300 K is only  $2.2 \times 10^{-4}$  and, furthermore, the curve shows a positive temperature dependence which is unlikely for this kind of system.

Mahan also recognized the importance of the long-range attractive potential and he developed the resonant  $V \rightarrow V$  energy exchange theory based on dipole-dipole interaction<sup>27</sup>. His theory gives

$$P = \frac{2\sqrt{2}C}{\hbar R^6} \left( \frac{\pi\mu}{8kT} \right)^{1/2} \quad (7)$$

where  $C = (1/3)(\mu_1)_{10}(\mu_2)_{01}$ . Here,  $(\mu_1)_{10}$  is the  $1 \rightarrow 0$  vibrational dipole matrix element for  $\text{H}^{79}\text{Br}$ . From the integrated infrared absorption

coefficient for HBr  $0 \rightarrow 1$  transition ( $34.8 \text{ cm}^{-2} \text{ atm}^{-1}$  at 300 K)<sup>28</sup>,  $C$  is calculated to be  $4.45 \times 10^{-40} \text{ erg cm}^3$ . The calculated probability curve using Mahan's equation is also shown in Fig. 1 and labelled as  $P_{\text{M}}$ . The probability at 300 K is 0.024 and it shows a very weak negative temperature dependence ( $P \propto T^{-1/2}$ ).

Sharma and Brau<sup>29</sup> also recognized the importance of the long-range dipole-dipole attraction and arrived at a slightly different formula.

$$P = \frac{4C^2\mu}{\hbar^2 R^{*4} kT} \quad (8)$$

The results obtained from this equation are also plotted in Fig. 1 and labelled as  $P_{\text{SB}}$ . The calculated probabilities are too low ( $8 \times 10^{-4}$  at 300 K) to explain the large experimental value and they show rather weak  $T^{-1}$  temperature dependence. Even inclusion of higher-order multipole interactions does not affect the probability very much<sup>30</sup>. A slightly different approach taken by Stephenson *et al.*<sup>31</sup> gives the same results as Sharma and Brau's results.

In summary, the "long-lived" collision model which characterizes the hydrogen bonding energy as the dominant long-range attractive term has been applied to the resonant  $V \rightarrow V$  energy transfer process  $\text{H}^{79}\text{Br}(v=1) + \text{H}^{81}\text{Br}(v=0) \rightarrow \text{H}^{79}\text{Br}(v=0) + \text{H}^{81}\text{Br}(v=1) + 0.38 \text{ cm}^{-1}$ . The calculated  $V \rightarrow V$  energy exchange probabilities show negative temperature dependence ( $P \propto T^{-1.8}$ ) over the temperature range studied. The agreement with the available experimental data is better than other resonant  $V \rightarrow V$  energy transfer theories.

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