

## Vibrational Relaxation of HF ( $v=3$ ) + CO

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### INTRODUCTION

In the vibrational energy transfer of molecules with excited vibrational levels, the strong attraction between the molecules increases the reaction rate of vibrational relaxation. In general, the vibrational energy transfer reaction between molecules with weak interaction occurs at a short distance, and thus the collision is affected by the repulsive potential and has a short reaction time. However, perturbation occurs in molecules with strong attraction when the molecules are relatively further apart, and thus the longer collision time allows energy transfer reaction.<sup>1</sup> For example, hydrogen halides such as HF and HCl have a high hydrogen bond energy, and their vibrational energy transfer mechanism differs from that of molecules with weak interaction. Hydrogen halides exhibit negative temperature dependence; the probability of energy transfer at a low temperature decreases with an increase in temperature. Owing to such a strong hydrogen bond (6 kcal/mole) at a lower temperature, HF molecules can form a nonrigid dimer with a longer lifetime, and thus the vibrational energy transfer between HF molecules occurs at a relatively long separation distance. Shin reported that in the near equilibrium configuration the HF molecules in the dimer undergo the hindered rotational motion and back-and-forth translational motion. This shows that the HF vibrational energy transfer from an excited vibrational level can occur via hindered rotational and/or translational motion.<sup>2,3</sup> Further, Shin suggested a long-lived collision model to calculate the vibrational energy transfer probability for HCl; this model assumes that the two collision reaction molecules maintain the reaction for a sufficiently long time at room temperature owing the hydrogen bond energy (2.1 kcal/mole) between the HCl molecules.<sup>4</sup> Lee et al. used Shin's long-lived collision model to explain the experimental results of the vibration-vibration energy transfer reaction in HF ( $v=n$ ) + H<sub>2</sub> ( $v=0$ ) and DF ( $v=n$ ) + D<sub>2</sub> ( $v=0$ ) reaction systems.<sup>5</sup>

Because the hydrogen bond energy between HF and CO

is significantly large (3.0 kcal/mole),<sup>6</sup> the vibrational energy relaxation in HF ( $v$ ) + CO reaction system has attracted much interest in numerous experimental and theoretical studies. Sirkin and Pimentel<sup>7</sup> predicted that the HF vibrational relaxation will mainly occur via the  $V$ - $R$  mechanism in the vibrational relaxation experiment of HF + CO system. Raybone et al. predicted that in the IR chemiluminescence experiment for the vibrational relaxation of HF ( $v=3$ ) + CO, the primary reaction pathway for relaxation reaction is  $V$ - $R,T$ , which is single vibrational quantum transition.<sup>8</sup> However, Dzelzkaln and Kaufman predicted that for the high vibrational relaxation energy levels of HF ( $v=5,6,7$ ) + CO,  $V$ - $V$  process would be the main mechanism for energy transfer.<sup>9</sup> Further, Wallis and Thompson used the quasiclassical trajectory method to calculate the vibrational relaxation rate for HF + CO reaction.<sup>10</sup>

In this study, Shin's long-lived collision model was used because the energy of hydrogen bond between HF and CO is 3.0 kcal/mole, which is sufficiently large. The rate constant for the vibrational energy relaxation of HF ( $v=3$ ) + CO reaction system was calculated using the  $V$ - $R$  mechanism. To obtain the rate constant for vibrational relaxation transfer, the interaction potential energy between two collision molecules was calculated using Morse-type equation. A two-dimensional collision model was used in the calculation, and the collision trajectory based on reaction time was calculated in terms of classical mechanics using Newton's equations of motion. The rate for  $V$ - $R$  energy transfer of HF molecules was calculated using the quantum mechanical method. Further, the calculated result was compared with the existing experimental and theoretical calculation data to demonstrate  $V$ - $R$  process as the mechanism for the vibrational relaxation in HF ( $v=3$ ) + CO reaction system.

### INTERACTION POTENTIAL

The equilibrium orientation of HF and CO in the dimer interacting *via* hydrogen bond energy was assumed to be

linear, and the interaction between the H in HF molecule and the C in CO molecule was considered. Then, the Morse potential equation stated below was used for the calculation.

$$V(r) = D \left[ \exp\left(\frac{r_e - r}{a}\right) - 2 \exp\left(\frac{r_e - r}{2a}\right) \right] \quad (1)$$

where,  $r$  is the distance between the H in HF and the C in CO, and  $r_e$  is the equilibrium distance between the two molecules.  $D$  and  $a$  are the Morse potential constants to be determined. In the current model,  $D$  is the energy of hydrogen bond between the two reactant molecules. If the relative distance between the mass centers of the two collision molecules,  $R$ , is much larger than the equilibrium bond distances of HF and CO,  $d_1$  and  $d_2$ , distance  $r$  between the two atoms H and C can be written as follows:

$$r \approx R - \gamma_1(d_1 + x_1)\cos\theta_1 + \gamma_2(d_2 + x_2)\cos\theta_2 \quad (2)$$

where,  $\gamma_1 = m_F/(m_H + m_F)$  and  $\gamma_2 = m_O/(m_C + m_O)$ .  $\theta$  is the angle between the molecular axis and  $R$ . The equilibrium distance between the two atoms H and C can be written as follows:  $r_e \approx R_e - \gamma_1 d_1 \cos\theta_{1e} + \gamma_2 d_2 \cos\theta_{2e}$ , where subscripts 1 and 2 refer to HF and CO molecules, respectively. Using Eq. (2) and the equation for equilibrium distance  $r_e$  on Eq. (1) and conducting a series expansion on the exponents with  $x_1$  and  $x_2$ , the overall interaction potential can be approximated as follows:

$$V(R, \theta_1, \theta_2, x_1, x_2) \approx V_0(R, \theta_1, \theta_2) + V_1(R, \theta_1, \theta_2, x_1) + V(R, \theta_1, \theta_2, x_2) \quad (3)$$

The first term in Eq. (3) can be rewritten for a potential term that includes only the relative translational motion between the two molecules in  $\theta_1$  and  $\theta_2$  orientation states as follows:

$$V_0(R, \theta_1, \theta_2) = D \left\{ [Q_1(\cos\theta_1 - \cos\theta_{1e}) - Q_2(\cos\theta_2 - \cos\theta_{2e})] \times \exp\left(\frac{R_e - R}{a}\right) - 2 \exp\left[\frac{1}{2}Q_1(\cos\theta_1 - \cos\theta_{1e}) - \frac{1}{2}Q_2(\cos\theta_2 - \cos\theta_{2e})\right] \exp\left(\frac{R_e - R}{2a}\right) \right\} \quad (4)$$

where,  $Q_1 = \gamma_1 d_1/a$  and  $Q_2 = \gamma_2 d_2/a$ . The second term of Eq. (3) can be rewritten for a potential term for  $V-R$  transition that assumes the vibrational-to-rotational energy transfer within HF molecule.

$$V_1(R, \theta_1, \theta_2, x_1) = \frac{D\gamma_1}{a} \left\{ \exp[Q_1(\cos\theta_1 - \cos\theta_{1e}) - Q_2(\cos\theta_2 - \cos\theta_{2e})] \exp\left(\frac{R_e - R}{a}\right) - \exp\left[\frac{1}{2}Q_1(\cos\theta_1 - \cos\theta_{1e}) - \frac{1}{2}Q_2(\cos\theta_2 - \cos\theta_{2e})\right] \times \exp\left(\frac{R_e - R}{2a}\right) \right\} x_1 \cos\theta_1 \quad (5)$$

The last term of Eq. (3),  $V_2(R, \theta_1, \theta_2, x_2)$  is the potential term for the  $V-R$  process of CO; this was not considered in this study.

To determine the translational motion trajectory for various molecular orientations for  $\theta_1$  and  $\theta_2$ , expressed as  $R(t)$ , Eq. (4) can be rewritten for the mean orientation for  $\theta_1$  and  $\theta_2$  as follows:

$$V_0(R) = (2\pi)^{-2} \int_0^{2\pi} \int_0^{2\pi} U_0(R, \theta_1, \theta_2) d\theta_1 d\theta_2 = D \left\{ I_0^2(Q_1) \exp[Q_1(\cos\theta_1 - \cos\theta_{1e}) - Q_2(\cos\theta_2 - \cos\theta_{2e})] \times \exp\left(\frac{R_e - R}{a}\right) - 2 I_0^2(Q_1/2) \exp\left[\frac{1}{2}Q_1(\cos\theta_1 - \cos\theta_{1e}) - \frac{1}{2}Q_2(\cos\theta_2 - \cos\theta_{2e})\right] \exp\left(\frac{R_e - R}{2a}\right) \right\} \quad (6)$$

where,  $I_0$  is the 0-order modified Bessel function. If  $R_e^*$  is the new equilibrium distance for the average orientation for  $\theta_1$  and  $\theta_2$ , at  $R = R^*$   $dV(R)/dR = 0$  and then Eq. (7) can be derived as follows:

$$\exp[(R_e - R_e^*)/2a] = \frac{I_0(Q_1/2)I_0(Q_2/2)}{I_0(Q_1)I_0(Q_2)} \exp\left(\frac{1}{2}Q_1 \cos\theta_{1e}\right) \times \exp\left(-\frac{1}{2}Q_2 \cos\theta_{2e}\right) \quad (7)$$

Further, using Eq. (7), Eq. (6) can be rewritten as follows:

$$V_0(R) = D^* \{ \exp[(R_e^* - R)/a] - 2 \exp[(R_e^* - R)/2a] \} \quad (8)$$

where,  $D^* = D[I_0^2(Q_1/2)I_0^2(Q_2/2)/I_0(Q_1)I_0(Q_2)]$ . When there is a strong interaction between two collision molecules due to hydrogen bonding by HF and CO, the molecules will mostly form a weak complex for the duration of the collision reaction near  $R = R^*$ . This is a clear contrast from the reactions where a strong repulsive potential causes a short-distance collision. Therefore, by taking the average for  $\theta_2$  orientation as  $(2\pi)^{-1} \int_0^{2\pi} V_1(R, \theta_1, \theta_2, x_1) d\theta_2$  using

Eq. (5) and conducting a series expansion on the exponents with  $R_e^* - R$ , equation (9) can be derived as follows:

$$V_1(R, \theta_1, x_1) = \frac{D\gamma_1}{a} \left\{ A \exp(Q_1 \cos \theta_1) - B \exp\left(\frac{1}{2} Q_1 \cos \theta_1\right) + \left[ 2A \exp(Q_1 \cos \theta_1) - B \exp\left(\frac{1}{2} Q_1 \cos \theta_1\right) \right] [(R_e^* - R)/2a] + \left[ 2A \exp(Q_1 \cos \theta_1) - \frac{1}{2} B \exp\left(\frac{1}{2} Q_1 \cos \theta_1\right) \right] \times [(R_e^* - R)/2a]^2 + \dots \right\} x_1 \cos \theta_1 \quad (9)$$

where,  $A = I_0^2(Q_1/2)I_0^2(Q_2/2)/I_0^2(Q_1)I_0(Q_2)$  and  $B = I_0(Q_1/2)I_0^2(Q_2/2)/I_0(Q_1)I_0(Q_2)$ . The first term of Eq. (9) is the potential for pure  $V-R$  energy transfer. The other terms of Eq. (9) refer to  $V-R, T$  process, where the vibrational energy of HF is transferred to rotational and translational motions. The current collision model considers  $V-R$  energy transfer, in  $R = R_e^*$  due to strong hydrogen bonding, to be the main process in a collision reaction. Therefore, the potential for  $V-R$  energy transfer can be expressed as follows:

$$V_1(\theta_1, x_1) = \frac{D\gamma_1}{a} \left[ A \exp(Q_1 \cos \theta_1) - B \exp\left(\frac{1}{2} Q_1 \cos \theta_1\right) \right] \times x_1 \cos \theta_1 \quad (10)$$

The introduction of Boson operators  $(\mathbf{a}^+, \mathbf{a})^{11}$  provides the coordinates of a reaction system,  $\hat{x}_1 = (\hbar/2M_1\omega_1)^{1/2}(\mathbf{a}^+ + \mathbf{a})$ , and thus Eq. (10) can be rewritten as follows:

$$V_1(\theta_1, x_1) = \frac{D\gamma_1}{a} \left[ A \exp(Q_1 \cos \theta_1) - B \exp\left(\frac{1}{2} Q_1 \cos \theta_1\right) \right] \times \left( \frac{\hbar}{2M_1\omega_1} \right)^{1/2} (\mathbf{a}^+ + \mathbf{a}) = F(t)(\mathbf{a}^+ + \mathbf{a}) \quad (11)$$

where,  $M_1$  and  $\omega_1$  are the reduced mass and angular frequency of HF, respectively.

### PROBABILITY EQUATION FOR VIBRATIONAL RELAXATION TRANSFER

The Hamiltonian for a collision reaction system expressed by Boson operators can be written as follows:

$$H = \frac{1}{2} \hbar \omega_1 (2\mathbf{a}^+ \mathbf{a} + 1) + F(t)(\mathbf{a}^+ + \mathbf{a}) = H^0 + H'(t) \quad (12)$$

where,  $H'(t) = F(t)(\mathbf{a}^+ + \mathbf{a})$  refers to the perturbation due to collision. The time-dependent Schrödinger equation for

a collision reaction system using Eq. (12) can be written as follows:

$$i\hbar \frac{\partial |\psi_v(t)\rangle}{\partial t} = [H^0 + H'(t)] |\psi_v(t)\rangle \quad (13)$$

The solution for this equation can be rewritten as follows:

$$|\psi_v(t)\rangle = \exp[G(t)(\mathbf{a}^+ + \mathbf{a})] |\psi_v(t)\rangle \quad (14)$$

where,  $G(t)$  is the imaginary function determined by the perturbation term  $H'(t)$  in Eq. (13) for time  $t$  as shown in Eq. (15).<sup>12</sup>

$$G(t) = -\frac{i}{\hbar} \int_{-\infty}^{+\infty} F(t) e^{i\Delta\omega t} \quad (15)$$

where,  $\Delta\omega = \Delta E/\hbar$ . The probability equation for the vibrational relaxation of HF from the initial vibrational state,  $v$ , to the final vibrational state,  $f$ , between the initial collision time,  $t = -\infty$ , and the final collision time,  $t = +\infty$ , can be written as follows:

$$P_{v \rightarrow f} = \lim_{t \rightarrow \infty} |\langle \psi_f(t) | \psi_v(t) \rangle|^2 = \langle \psi_f(t) | \exp[G(t)(\mathbf{a}^+ + \mathbf{a})] | \psi_v(t_0) \rangle|^2 \quad (16)$$

For Eq. (16), a rotational motion trajectory to obtain the transfer probability,  $\theta_1(t) = \Omega t + \theta_0$ , was used. Here,  $\Omega$  is the angular frequency of rotational motion,  $(2E_r/I)^{1/2}$ , and  $I$  is the inertia moment. Using Eq. (16), the transfer probability equation for temperature ( $T$ ) considering Boltzmann distribution can be expressed as follows:

$$P_{v \rightarrow f}(T) = (kT)^{-1} \int_0^\infty P(E_r) \exp(-E_r/kT) dE_r \quad (17)$$

where,  $k$  is Boltzmann constant.

### CALCULATIONS AND RESULTS

The potential constants<sup>6</sup> used to calculate the vibrational relaxation probability using Eq. (17) are  $D = 3.0$  kcal/mole and  $a = 2.0$  Å. The spectroscopic data of HF and CO were obtained from the standard table.<sup>13</sup> The vibrational energy transfer reaction of HF from the collision with CO is an exothermic reaction, where the vibrational energy is relaxed from a high to a low vibrational energy. Therefore, considering the imbalance from vibrational relaxation energy,  $\Delta E$ , to transfer to rotational energy level before and after the collision,  $E_r^* = [(E_r + \Delta E)^{1/2} + E_r^{1/2}]^2/4$  was used as the rotational energy. The rate constant to compare the theoretical value obtained using Eq. (17) and the experimental values

of vibrational relaxation transfer probability of HF ( $v=3$ ) + CO reaction system are as follows:

$$k_d(T) = ZP_{v \rightarrow f}(T) \\ = 4.74 \times 10^{10} r^* (T\mu^*)^{-1/2} P_{v \rightarrow f}(T) \text{ atm}^{-1} \cdot \text{sec}^{-1} \quad (18)$$

Here, subscript “d” on rate constant,  $k_d$ , shows that this is a nonrigid collision model, and  $\mu^*$  is the reduced mass written as atomic mass unit (amu). For collision radius,  $r^* = 3.069 \text{ \AA}$  was selected.<sup>6</sup> By substituting the values of  $\mu^*$  and  $r^*$  in Eq. (18) and multiplying  $RT$  the rate constant with  $\text{cm}^3/\text{molecule-s}$  as the unit can be expressed as follows:

$$k_d(T) = 1.81 \times 10^{-11} T^{1/2} P_{v \rightarrow f}(T) \text{ cm}^3/\text{molecule-s} \quad (19)$$

Using Eq. (19), at 300 K the rate constant for vibrational energy transfer,  $k_d$  in HF ( $v=3$ ) + CO  $\rightarrow$  HF ( $v=2$ ) + CO +  $\Delta E$  reaction systems was calculated. Table 1 shows the result along with other experimental and theoretical calculation results. The calculated value using Eq. (19), was  $k_d = 2.20 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$ , which corresponds to the other experimental and theoretical values. As shown in Table 1, the rate constant,  $3.0 \text{ cm}^3/\text{molecule-s}$ , calculated using the quasiclassical trajectory method has a larger  $k_d$  value than our calculations, even though the difference is small. The experimental values are 2.5, 2.8, and  $2.9 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$ . These values are not significantly different, but are also slightly higher than our calculations. This is probably because only  $V-R$  was considered rather than both the competitive pathways,  $V-R$ ,  $T$  and  $V-R$ , in the calculations of HF vibrational relaxation reaction. The current calculation, which only considered the  $V-R$  mechanism, corresponds to the other experimental and theoretical calculation results, indicating that HF ( $v=3$ ) + CO vibrational relaxation reaction mainly occurs via the  $V-R$  reaction pathway. Indeed, all the interaction potential terms related to  $V-R$ ,  $T$ , including the term  $(R_e^* - R)/2a$ , in Eq. (9) were excluded,

**Table 1.** Rate constants<sup>a</sup> for the vibrational relaxation of HF ( $v=3$ ) + CO and HF ( $v=2$ ) + CO at 300 K

This work	Willis-Thompson <sup>b</sup>	Experiment
$2.20 \times 10^{-12}$	$(3.0 \pm 1.2) \times 10^{-12}$	$(2.9 \pm 3.0) \times 10^{-12c}$
		$(2.8 \pm 0.2) \times 10^{-12d}$
		$(2.5 \pm 0.3) \times 10^{-12e}$

<sup>a</sup>Rate constants have units of  $\text{cm}^3/\text{molecule-s}$ .

<sup>b</sup>Reference 10.

<sup>c</sup>References 15 and 16.

<sup>d</sup>Reference 8.

<sup>e</sup>Reference 17.

and only the 0-order term for  $(R_e^* - R)/2a$  obtained through the series expansion of  $\exp[(R_e^* - R)/2a]$  was used for the vibrational relaxation transfer rate constant,  $k_d$ , calculation for HF. In other words, the  $V-R$  mechanism that does not include the transfer of vibrational relaxation energy to the internal translational motion energy is the process, when HF and CO are in  $R = R_e^*$  where molecules exist in weakly bonded dimer via hydrogen bonding, in which the vibrational relaxation energy  $\Delta E$  is transferred to the internal rotational energy of HF when the vibrational level of HF is transferred from  $v=3$  to 2. Further, the vibrational relaxation reaction of HF owing to CO is an exothermic reaction with a high  $\Delta E$  ( $3624 \text{ cm}^{-1}$ ). In general, as  $\Delta E$  increases in vibrational energy transfer reaction, it is more efficient to transfer the  $\Delta E$  to a rotational motion level rather than an internal translational motion.<sup>14</sup> Therefore, the calculation results show that the relaxation transfer reaction is a  $V-R$  process, where the relaxed vibrational energy of HF molecule is transferred to the internal rotational level rather than  $V-R$ ,  $T$  process.

The current  $k_d$  obtained from the  $V-R$  reaction pathway is a calculation result that assumes HF as a harmonic oscillator. In other words, for the wave functions of HF in the matrix term of Eq. (16), the wave functions of harmonic oscillators were used. For example, when HF undergoes vibrational relaxation from  $v=3$  to  $v=2$ , the series expansion of the exponent in Eq. (16) results in a probability equation for the vibrational relaxation of HF as shown below.

$$P_{3 \rightarrow 2}(E_r) = |\langle \psi_2(t) | 1 + G(t)(\mathbf{a}^+ + \mathbf{a}) | \psi_3(t) \rangle|^2 \quad (20)$$

If wave functions  $\psi_2$  and  $\psi_3$  are harmonic oscillator wave functions with vibrational levels 2 and 3, respectively, the first and second terms of Eq. (20) are  $\langle \psi_2(t) | \psi_3(t) \rangle = 0$  and  $\langle \psi_2(t) | (\mathbf{a}^+ + \mathbf{a}) | \psi_3(t) \rangle = \sqrt{3}$ . Here, the calculations for Boson operators used  $\mathbf{a}^+ \psi_n = (n+1)^{1/2} \psi_{n+1}$  and  $\mathbf{a} \psi_n = n^{1/2} \psi_{n-1}$ . However, if wave functions  $\psi_2$  and  $\psi_3$  are anharmonic oscillator functions, the terms are  $\langle \psi_2(t) | \psi_3(t) \rangle = 0$  and  $\langle \psi_2(t) | (\mathbf{a}^+ + \mathbf{a}) | \psi_3(t) \rangle = 2.65$ . The anharmonic oscillator wave function  $\psi_n(t)$  used in the calculation is shown below.

$$\psi_n(t) = \varphi_n + \frac{K}{6\sqrt{2}} \{ [(n+1)(n+2)(n+3)]^{1/2} \varphi_{n+3} \\ + 9(n+1)^{3/2} \varphi_{n+1} - 9n^{3/2} \varphi_{n-1} - [n(n-1)(n-2)]^{1/2} \varphi_{n-3} \} \quad (21)$$

where,  $K = (\alpha/\hbar\omega)(\hbar/m\omega)^{3/2}$ , and  $\varphi$  is the harmonic oscillator wave function in vibrational level,  $i$ . Moreover,  $\alpha = -b^3 D_e$  and  $b = \omega_e(2\pi^2 c \mu / D_e \hbar)^{1/2}$ .  $D_e$  is the equilib-

rium dissociation energy of the oscillator. The vibrational relaxation rate constant,  $k_d$ , for the  $V$ - $R$  process was calculated using the anharmonic oscillator wave function given in Eq. (21), which is  $5.15 \times 10^{-12}$  cm<sup>3</sup>/molecule-s. This is approximately twice the value obtained from the calculation assuming HF as a harmonic oscillator. As shown above, this is because of the value of  $\langle \psi_2(t) | (\mathbf{a}^+ + \mathbf{a}) | \psi_3(t) \rangle$  with  $\sqrt{3}$  and 2.65 differences when harmonic and anharmonic oscillator wave functions, respectively, are used. In general, HF molecules are anharmonic, and thus  $k_d$  probably has an anharmonic factor. However, in reality, the result as the harmonic oscillator provided closer values to the experimental data.

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