

문자간 상호작용과 에너지이동에 대한 이론적 연구 ;  
높은 振動準位로 들뜬 HF 및 DF 의 振動緩和

李昌淳 · 李民柱 · 金裕恒<sup>†</sup>  
仁荷大學校 理科學 化學科  
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Intermolecular Interaction and Molecular Energy Transfer;  
Vibrational Relaxation of Highly Excited HF and DF

Chang Soon Lee, Min Joo Lee and Yoo Hang Kim  
Department of Chemistry, Inha University, Incheon 160, Korea  
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**요약.** HF ( $v=5-7$ ) 및 DF ( $v=9-12$ )의 HF ( $v=0$ ) 및 DF ( $v=0$ )에 의한 전체 진동완화 속도 상수  $k_{v, v-1}$ 을 진동-진동 ( $V \rightarrow V$ ) 및 진동-회전, 병진 ( $V \rightarrow R, T$ ) 두 반응경로를 모두 다 고려하여 단순한 충돌모형과 반고전적 계산방법을 써서 계산하였다. 계산된 속도상수들은 실험값 및 다른 이론들로부터 계산한 값들과 비교적 잘 맞았고, 온도 및 양자수  $v$ 가 커짐에 따라 증가하였다. 또한 높은 진동 준위로 들뜬 HF 및 DF의 진동완화과정은 저온에서는 거의 다  $V \rightarrow R, T$  경로로 일어나며 온도가 올라감에 따라  $V \rightarrow V$  경로의 중요성이 커짐을 보였다.

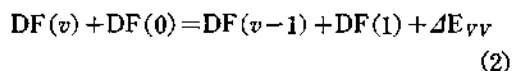
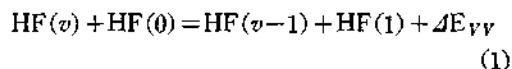
**ABSTRACT.** The total vibrational deexcitation rate constants  $k_{v, v-1}$  of HF ( $v=5-7$ ) by HF ( $v=0$ ) and DF ( $v=9-12$ ) by DF ( $v=0$ ) including both the vibration to vibration ( $V \rightarrow V$ ) and vibration to rotation and translation ( $V \rightarrow R, T$ ) energy transfer channels have been calculated semiclassically using a simplified collision model. The calculated results are in reasonably good agreement with those obtained by experimental and other theoretical studies. The rate constants increase with increasing temperature and also with increasing  $v$ . They also show that the relaxation of the highly excited HF and DF occurs predominantly via the  $V \rightarrow R, T$  path at low temperature. The effectiveness of the  $V \rightarrow V$  path, however, increases as the temperature is raised.

### 1. INTRODUCTION

The relaxation of vibrationally excited hydrogen fluoride molecules, both HF and DF, continues to be of interest due to the important role played by these molecules in chemical lasers and theoretical understanding of the fundamental, microscopic kinetic processes.<sup>1</sup>

Recently, the emphasis in this field of study has been shifted to the vibrational deexcitation mechanism of the highly excited species.<sup>2-13</sup> In

the vibrational relaxation of the excited HF and DF, there are two competing reaction channels. One is the relaxation through the vibration to vibration ( $V \rightarrow V$ ) energy transfer processes:



The other is relaxation through the vibration to rotation and translation ( $V \rightarrow R, T$ ) energy

transfer processes:

$$HF(v) + HF(0) = HF(v-1) + HF(0) + \Delta E_{VR} \quad (3)$$

$$DF(v) + DF(0) = DF(v-1) + DF(0) + \Delta E_{VR} \quad (4)$$

In the  $V \rightarrow V$  processes (Eqs. 1 and 2) only the energy mismatch  $\Delta E_{VV}$ , that is, the small vibrational energy difference between the deexcited and excited molecule is transferred to the rotational and/or translational motion of the collision system. On the other hand, in the  $V \rightarrow R, T$  processes (Eqs. 3 and 4), one whole vibrational quantum  $\Delta E_{VR}$  is transferred to the rotational and/or translational motion of the quencher molecule.

The experimental results show that the one-quantum vibrational deexcitation rate constants  $k_{v, v-1}$  display surprisingly strong quantum number ( $v$ ) dependence and become very large for high  $v$  and that the relaxation mechanism proceeds predominantly via  $V \rightarrow R, T$  process rather than via  $V \rightarrow V$  process.<sup>2</sup>

These results are rather surprising since, for the vibrational relaxation of low-lying excited states, it is generally recognized that the  $V \rightarrow V$  path is much more preferred to the  $V \rightarrow R, T$  path. For example, for  $v=2$ , the  $V \rightarrow V$  fraction ( $f_{VV}$ ) obtained by laser double resonance technique<sup>14</sup> and fast flow infrared chemiluminescence experiment<sup>4</sup> is 0.6~0.8 and 0.55, respectively. Sophisticated trajectory calculations predict it to be between 0.58 and 0.94<sup>11~13</sup> and the scaling theory also predicts its value as 0.65.<sup>15</sup> Previously, Shin and Kim<sup>16</sup> reported the temperature dependence of the deexcitation rates of HF for  $v=2$  to 5 and Shin<sup>17</sup> reported that of DF for  $v=2$  to 5 considering only the  $V \rightarrow V$  energy transfer channel. In this work, we extend this model to the higher vibrational states of HF ( $v=5$  to 7) and DF

( $v=9$  to 12) and include the  $V \rightarrow R, T$  relaxation processes too in the calculation of the total deexcitation rate constants  $k_{v, v-1}$

## 2. COLLISION MODEL AND ENERGY TRANSFER PROBABILITY

### 2-1. $V \rightarrow V$ Energy Transfer

Shin and Kim proposed two possible mechanisms for the  $V \rightarrow V$  energy transfer processes; one is through the formation of dimers at low temperatures in which the small energy mismatch is transferred to the back-and-forth translational motion of the collision system, and the other is that in which this energy is transferred to the rotational motion of the colliding system.<sup>16</sup> The former, the so-called dimer formation mechanism, is valid only at lower temperatures. Furthermore, its contribution to the total  $V \rightarrow V$  energy transfer process rapidly decreases as  $v$  becomes larger.<sup>16,17</sup> Since we are interested both in the relatively high temperature range from 300 to 2000 K and in the higher vibrational states, we ignore this mechanism and consider only the latter mechanism and hereafter designate it as  $V \rightarrow V$  process.

The collision model and derivation of the energy transfer probability for this  $V \rightarrow V$  process are given elsewhere,<sup>16,18</sup> so we quote the final equation for vibrational relaxation probability of HF as follows:

$$P_{v, v-1}^{V \rightarrow V}(T) = 4 \langle v-1, 1 | (\mathbf{a}_1^+ + \mathbf{a}_1) (\mathbf{a}_2^+ + \mathbf{a}_2) | v, 0 \rangle^2 \cdot \left[ 1 - 2K(1-K) \left( 1 + \frac{\Delta E_{VV}}{2kT} \right) + K^2 \left( \frac{\Delta E_{VV}}{2kT} \right)^2 \right] \left( \frac{\pi \Delta E_{VV} \phi_1}{\hbar \omega} \right)^2 (1+\alpha)^4 \left[ 1 - \frac{\hbar}{2(1+\alpha) \Delta E_{VV}} \left( \frac{Dq_F}{adM} \right)^{\frac{1}{2}} \frac{\phi_2}{\phi_1} \right] \cdot \exp \left\{ -\frac{3\chi}{kT} + \frac{4(D\chi)^{\frac{1}{2}} g}{\pi kT} + \frac{16Dg^2}{3\pi^2 kT} - \frac{\Delta E_{VV}}{2kT} \right\} \quad (5)$$

where

$$\phi_1 = \frac{\cosh(Q_2) + \cosh(Q_1)}{\sinh(Q_2) + (Q_2/Q_1)\sinh(Q_1)} - \frac{1}{Q_2} \quad Q_{1,2} = q_{H,F}d/a, \quad q_{H,F} = m_{H,F}/m_{HF},$$

$$\phi_2 = \frac{\cosh(Q_2/2) + \cosh(Q_1/2) - (2/Q_2)[\sinh(Q_2/2) + (Q_2/Q_1)\sinh(Q_1/2)]}{[\sinh(Q_2) + (Q_2/Q_1)\sinh(Q_1)]^{1/2}}$$

$$\alpha = \frac{9}{2Q_2^2} \left[ 1 + \frac{4}{3Q_2^2} \right]$$

$$K = t^*kT/\omega\mu a^2,$$

$$t^* = \pi(I/2E^*)^{1/2}\alpha_0 \left[ 1 - \frac{2}{\pi}(D/E^*)^{1/2}g \right]$$

$$\alpha_0 = \frac{(1+\alpha)a}{q_F d}, \quad E^* = \chi - \left( \frac{8g}{3\pi} \right) (D/\chi)^{1/2}$$

$$\chi = [(M/2q_F)^{1/2}(\Delta E_{VR}/\hbar)\pi(1+\alpha)akT]^{2/3},$$

and

$$g = \frac{2^{1/2} [Q_2^{-1}\sinh(Q_2/2) + Q_1^{-1}\sinh(Q_1/2)]}{[Q_2^{-1}\sinh(Q_2) + Q_1^{-1}\sinh(Q_1)]^{1/2}}$$

Here,  $\alpha^+$  and  $\alpha$  are phonon creation and annihilation operators, respectively,<sup>19</sup>  $\omega$  the fundamental vibrational frequency,  $D$  the attractive energy between the two rotating HF molecules,  $a$  the potential range parameter,  $M$  the reduced mass of the molecule,  $m_H$  the mass of the hydrogen atom,  $\mu$  the reduced mass of the collision system, and  $d$  the internuclear distance of the molecule.

## 2-2. $V \rightarrow R, T$ Energy Transfer

The probability of vibrational deexcitation for  $v=1 \rightarrow 0$  process through the  $V \rightarrow R, T$  energy transfer mechanism in which one whole vibrational quantum of energy is transferred to the rotational and translational motion of the quencher is given elsewhere.<sup>20, 21</sup> Modifying this probability equation to take the relaxation of high vibrational states into account, one obtains

$$P_{v=1 \rightarrow 0}^{V \rightarrow R, T}(T) = \langle v-1 | (\alpha^+ + \alpha) | v \rangle^2 \\ C f_{VT}(T) (4\pi/3)^{1/2} (\chi'/kT)^{1/2} \\ \exp \left[ -\frac{3\chi'}{kT} + \frac{8(g'D\chi')^{1/2}}{kT} + \frac{64g'D}{3\pi^2 kT} + \frac{\Delta E_{VR}}{2kT} \right] \quad (6)$$

where

$$C = \frac{8}{M\hbar\omega} \left( \frac{\Delta E_{VR}\pi I a}{\hbar d^2} \right)^2 \left( \frac{a}{q_F d} \right)^2 (1+\alpha)^4 \\ \left[ 1 - \frac{q_F d}{a} \coth(q_F d/a) \right]^2 \left\{ 1 - \frac{4\sinh(q_F d/2a)}{[\sinh(q_F d/a)]^{1/2}} \right\}$$

$$\cdot \frac{[1 - (q_F d/2a) \coth(q_F d/2a)]}{[1 - (q_F d/a) \coth(q_F d/a)]} \\ \left( \frac{8Dd}{Ia} \right)^{1/2} \frac{\hbar}{(1+\alpha)\Delta E_{VR}} \Bigg\}^2$$

$f_{VT}(T) = [1 - 2(K/A) + 2(K/A)^2]/A$ , which represents the effect of translational motion,

$$A = 1 - \frac{\pi^2}{12} (1+\alpha)^2 (m_H/\mu),$$

$$g' = \left( \frac{a}{q_F d} \right) \frac{\sinh^2(q_F d/2a)}{\sinh(q_F d/a)}$$

and

$$\chi' = \left[ \left( \frac{M}{2q_F} \right)^{1/2} \pi(1+\alpha)akT \left( \frac{\Delta E_{VR}}{\hbar} \right) \right]^{2/3}$$

## 2-3. Vibrational Relaxation Rate Constants

Once the energy exchange probabilities are known, the rate constants can be obtained from the gas kinetics as follows,

$$k = ZP(T) \\ = 4.74 \times 10^{10} r^2 (T\mu)^{-1/2} P(T) \quad (7)$$

where  $Z$  is the collision number,  $r$  the collision diameter in Å, and  $\mu$  the reduced mass of the collision system expressed in atomic mass unit. The resulting rate constants in Eq. (7) are expressed in  $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$ .  $P(T)$  is the sum of  $V \rightarrow V$  and  $V \rightarrow R, T$  transition probabilities.

## 3. CALCULATION

Even though the collision trajectory used in this work has been obtained classically, the diatomic molecules HF and DF are treated quantum mechanically. Furthermore, since we are dealing with the high vibrational states, the anharmonicity effect must be taken into account in calculating the matrix elements and energy differences. According to the first order perturbation theory, the vibrational wave func-

tion of anharmonic oscillator with potential energy  $V(x) = M\omega^2 x^2/2 + \beta x^3$  can be given as<sup>22</sup>.

$$\begin{aligned} \phi_v = \phi_v + \frac{B}{6\sqrt{2}} & \{ [(v+1)(v+2)(v+3)]^{1/2} \phi_{v+3} \\ & + 9(v+1)^{3/2} \phi_{v+1} - 9v^{3/2} \phi_{v-1} \\ & - [v(v-1)(v-2)]^{1/2} \phi_{v-3} \} \end{aligned} \quad (7)$$

where  $x$  is the vibrational amplitude,  $\phi_v$ 's are harmonic oscillator wave functions and  $B$  is the constant given as  $(\beta/\hbar\omega)(\hbar/M\omega)^{3/2}$ .

The anharmonicity constant  $\beta$  can be obtained from the expansion of the experimental Morse potential,  $V(x) = D_e[1 - \exp(-bx)]^2$  and is found to be  $-D_e b^3$ . The parameters apart from the atomic masses and the universal constants used in the calculation are as follows:

$d = 0.917 \text{ \AA}$ ,<sup>24</sup>  $D = 400 \text{ K}$ ,<sup>25</sup>  $D_e = 141 \text{ kcal/mol}$ ,  $b = 2.232 \text{ \AA}^{-1}$ ,<sup>26,27</sup>  $\omega(\text{HF}) = 4138.52 \text{ cm}^{-1}$  and  $\omega(\text{DF}) = 2998.25 \text{ cm}^{-1}$ .<sup>24,28</sup> The energy difference for both the  $V \rightarrow V$  and  $V \rightarrow R$ ,  $T$  relaxation processes are given in Table 1. The collision diameter  $r$  is assumed to be as  $2.79 \text{ \AA}$ .<sup>29</sup> The repulsive potential range parameter  $a$  varies from  $0.202 \text{ \AA}$  at  $300 \text{ K}$  to  $0.183 \text{ \AA}$  at  $2000 \text{ K}$ .<sup>23</sup>

#### 4. RESULTS AND DISCUSSION

The calculated total vibrational relaxation rate constants  $k_{v,v-1}$  including both the  $V \rightarrow V$  and  $V \rightarrow R$ ,  $T$  contributions for HF ( $v=5-7$ ) and DF ( $v=9-12$ ) are collected in Tables 2 and 3, respectively along with other available experimental and theoretical results at  $300 \text{ K}$ . For HF, as can be seen from Table 2, our calculated rate constants agree reasonably well with those obtained from other studies. For DF, the agreement between the calculated values from this work and those obtained experimentally is good when  $v$  is small and poor when  $v$  is large. However, in view of the very wide scatter of the experimental data for HF, it may be too early to judge the validity of this model with only one set of experimental data for DF.

Table 1. Amount of energy transferred

| Process( $v$ ) | $E_{VV}(\text{cm}^{-1})$ | $E_{VR}(\text{cm}^{-1})$ |
|----------------|--------------------------|--------------------------|
|                | HF                       |                          |
| 5→4            | -663*                    | 3299                     |
| 6→5            | -819                     | 3143                     |
| 7→6            | -973                     | 2989                     |
|                | DF                       |                          |
| 9→8            | -684                     | 2223                     |
| 10→9           | -764                     | 2142                     |
| 11→10          | -845                     | 2061                     |
| 12→11          | -925                     | 1961                     |

\*The minus sign signifies the endothermicity.

Table 2. Deexcitation Rate Constants\* for HF ( $v=5-7$ ) by HF at  $300 \text{ K}$

|             | $v=5$           | $v=6$         | $v=7$         | Ref.      |
|-------------|-----------------|---------------|---------------|-----------|
| Experiments | 3.9             |               |               | 6         |
|             | $0.52 \pm 0.30$ |               |               | 7         |
|             | $9.1 \pm 0.5$   |               |               | 9         |
|             | $9.0 \pm 0.6$   |               |               | 10        |
|             | 3.5             | 6.1           |               | 3         |
| Theory      | 2.8             | 3.1           | 2.6           | 8         |
|             | 8.4             | 18            | 27            | 3         |
|             | 1.9             |               |               | 30        |
|             | 2.5             | 3.1           |               | 12        |
|             | $1.6 \pm 0.6$   | $2.6 \pm 0.9$ | $4.9 \pm 1.7$ | 11        |
|             | $3.8 \pm 0.4$   | $8.2 \pm 0.8$ | $33 \pm 4$    | 13        |
|             | 4.7             | 13            | 36            | This work |

\*In  $10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ .

Table 3. Deexcitation Rate Constants\* for DF ( $v=9-12$ ) by DF at  $300 \text{ K}$

|            | $v=9$ | $v=10$ | $v=11$ | $v=12$ | Ref.      |
|------------|-------|--------|--------|--------|-----------|
| Experiment | 12    | 14     | 20     | 26     | 2         |
| Theory     | 14    | 29     | 61     | 150    | This work |

\*In  $10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ .

In Fig. 1 and 2, the temperature dependences of the calculated total vibrational rate constants of HF and DF are shown, respectively. As is evident from both figures, the rate constants increase as the temperature goes higher. This is because the long range attractive forces such

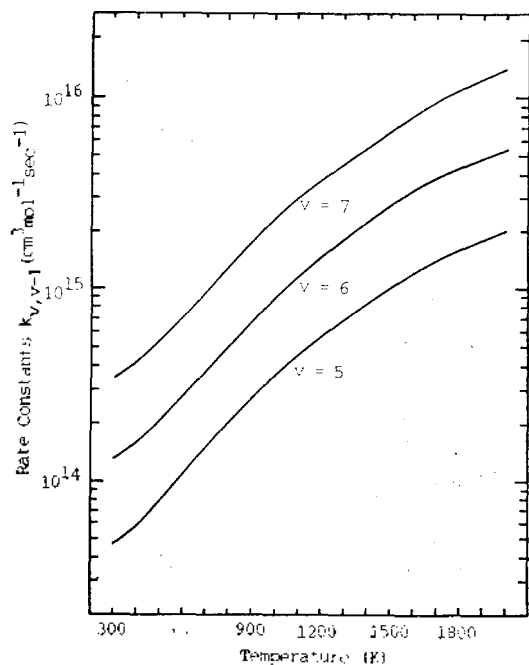


Fig. 1. Total Vibrational Deexcitation Rate Constants of HF( $v$ ) by HF for  $v=5-7$ .

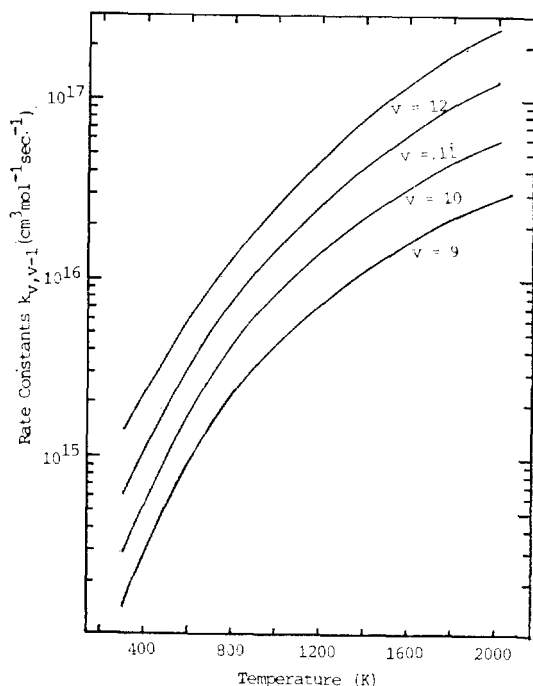


Fig. 2. Total Vibrational Deexcitation Rate Constants of DF( $v$ ) by DF for  $v=9-12$ .

Table 4. Percent Contribution of  $V \rightarrow V$  Energy Transfer Channel to the Total Vibrational Relaxation of HF ( $v=5-7$ ) by HF at 300K

|            | $v=5$    | $v=6$    | $v=7$    | Ref.      |
|------------|----------|----------|----------|-----------|
| Experiment | $\sim 0$ | $\sim 0$ | $\sim 0$ | 4         |
| Theory     | 8        | 2        | 0        | 11        |
|            | 8        | 4        | ...*     | 12        |
|            | 11       | 2        | 0        | 13        |
|            | 0        | ...      | ...      | 15        |
|            | 79       | ...      | ...      | 30        |
|            | 19       | 6        | 2        | This work |

\*Not given.

Table 5. Percent  $V-V$  Fraction for Vibrational Relaxation of HF( $v=5$ ) by HF at Several Temperatures

| 300K | 500K | 700K | 1000K | 2000K | Ref.                              |
|------|------|------|-------|-------|-----------------------------------|
| 7.6  | 6.1  | 6.4  | 5.7   | ...*  | Wilkins and Kwok <sup>12</sup>    |
| 8    | 27   | 39   | ...   | ...   | Billing and Poulsen <sup>11</sup> |
| 19   | 40   | 56   | 56    | 43    | This work                         |

\*Not given.

as hydrogen bond energy and dipole-dipole interaction terms are not included in the interaction potential between the two molecules. These orientation dependent long-range forces are not expected to play a significant role when the molecules undergo rapid rotational motion as in this model.<sup>16</sup>

The rate constants also increase as  $v$  becomes larger. This trend is in agreement with most of the experimental results<sup>2,3</sup> and also with other theoretical prediction.<sup>11,12</sup>

Next we consider the relative importance of the two competing energy transfer channels,  $V \rightarrow V$  and  $V \rightarrow R, T$ , in inducing vibrational relaxation. In Table 4 are listed the percent contributions of the  $V \rightarrow V$  channel to the total vibrational relaxation of HF at 300K. Our results are in good agreement with those from other theoretical studies except the very high value obtained from the information theory ann-

lysis of clending *et al.*<sup>20</sup> and they support the experimental finding that the relaxation of the higher vibrational states occurs predominantly via  $V \rightarrow R, T$  path. For DF,  $V \rightarrow V$  channel fractions at 300K are 34, 18, 5 and 2% for  $v=9, 10, 11$  and 12, respectively. Even though these values are larger for DF than for HF, the general characteristics are the same. That is, in both molecules,  $V \rightarrow R, T$  process dominates over  $V \rightarrow V$  process and this trend is more pronounced for larger  $v$ .

As the temperature is raised, however, the effectiveness of the  $V \rightarrow V$  channel generally increases as shown in Table 5 for the case of HF ( $v=5$ ). The endothermic character and exothermic character of the  $V \rightarrow V$  and  $V \rightarrow R, T$  processes given in Table 1 are represented as the last term in the exponent of Eq. 5 and 6, respectively. As the temperature becomes higher, these two terms also become smaller, thus resulting in increase of the  $V \rightarrow V$  fraction. It is interesting to note that our results are qualitatively in line with those of Billing and Poulsen<sup>11</sup> and contradict those of Wilkins and Kwok.<sup>12</sup> To decide which trend is right, a temperature dependent experimental study is highly desirable.

In summary, the total relaxation rate constants for the vibrational deexcitation of HF and DF including both the  $V \rightarrow V$  and  $V \rightarrow R, T$  channels have been calculated. Even though the collision model used in this study is very simple, it can explain essential features of the vibrational relaxation of the highly excited hydrogen fluoride molecules.

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