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Model of Hydrogen-Bond Interactions near the Equilibrium Configuration. Application to Vibrational Energy Transfer in DF($v = n$) + DF($v = 0$)[1a]

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Abstract: A model is developed in order to study near-equilibrium behavior of hydrogen-bond systems, in which individual molecules are considered to undergo hindered rotational motion and back-and-forth translational motion. The hindered rotational motion is described quantum mechanically, while the translational motion is analyzed in classical dynamics. Application of the model is made to calculate energy transfer probabilities of DF($v = n$) + DF($v = 0$) $\rightarrow$ DF($v = n - 1$) + DF($v = 1$) + ΔE for n = 2-5 at low temperatures, where the energy mismatch ΔE is transferred to the back-and-forth translational motion. As temperature increases, the formation of hydrogen bonds becomes less important, and energy transfer probabilities decrease sharply. The model is extended for the discussion of the self-deexcitation process DF($v = 1$) + DF($v = 0$) $\rightarrow$ DF($v = 0$) + DF($v = 0$) + ΔE at low temperatures, where ΔE is large and is now considered to be transferred to both the hindered rotational motion and back-and-forth translational motion. The model gives a strong negative temperature dependence of the deexcitation probability, which is in agreement with experiment.

The formation of hydrogen bonds is involved in many important phases of chemical and physical processes.[2-4] Hydrogen bonding in molecules such as H_2O, HF, and NH_3 is responsible for many of their most important properties and is quite common in proteins because of the presence of the carbonyl oxygen and amine hydrogen in the polypeptide chain. Unless they are formed between molecules in the rigid state, the molecules can have a significant degree of freedom in the near-equilibrium configuration. Then, such nonrigid bonds can affect the dynamic properties of molecules in restricted states of dimers. In a nonrigid dimer or an associated molecule, in addition to the vibrational motion of each molecule, two molecules can undergo restricted motion: namely, hindered rotational motion and restricted back-and-forth translational motion. The dynamics of these types of motion can be analyzed with the limited use of mathematics, and the information obtained from the analysis can be particularly useful in understanding processes which are associated with the formation of hydrogen bonds. One such process is the transfer of vibrational energy in collisions involving hydrogen fluorides at low temperatures where strong hydrogen-bond attraction can act between the molecules.[5]

The current interest in elementary processes taking place in chemical lasers has generated a need for kinetic information concerning energy transfer steps that govern excited state lifetimes.[6] Vibrationally excited deuterated fluoride molecules are known to undergo efficient vibration-vibration energy transfer with other molecules such as CO_2 thus producing, for example, $CO_2(00^\circ1)$ which, as a basis of lasing, converts chemical energy to coherent radiation energy. It is then important to know how vibrationally excited hydrogen fluoride molecules undergo deactivation. Since strong attractive forces act between the molecules, the energy transfer between DF($v = n$) and other DF molecules becomes an important process for the relaxation of such excited species.

In the present paper we shall develop a nonrigid dimer model by deriving the hydrogen-bond interaction energy near the equilibrium configuration. From experimental[7-9] and ab initio[10-13] studies the equilibrium configuration and the strength of the hydrogen bond are known, thus enabling us to determine the interaction energy as a function of pertinent intermolecular coordinates. We shall then discuss the dynamics of the restricted translational motion in the nonrigid structure and the quantum mechanical behavior of the hindered-rotational (small-amplitude oscillatory) motion of each molecule in the dimer. The idea will then be applied to calculate vibration-vibration energy transfer probabilities of DF($v = n$) + DF($v = 0$) $\rightarrow$ DF($v = n - 1$) + DF($v = 1$) + ΔE at low temperatures with the mechanism that the energy mismatch ΔE is transferred to the back-and-forth translational motion. The result will then be compared with that obtained from the complete rotational motion. The dimer model will also be applied to formulate the probability of the self-deactivation of hydrogen fluorides. Since the dimer model has already been introduced in ref 5, we shall briefly outline the derivation of pertinent expressions in the following section, but throughout the paper special emphasis will be given to a complete, rigorous discussion of the model and its application to molecular collisions.

Nonrigid Hydrogen-Bond Interaction

For two hydrogen fluoride molecules (HF or DF) forming a loosely bound nonrigid dimer at low temperatures, we can define the intermolecular coordinates as shown in Figure 1. The intermolecular atom-atom distances are complicated functions of r, θ_1, θ_2, and ϕ, but for the relative separation r significantly greater than the equilibrium bond distance d the atom-atom distances can be obtained in simpler forms. Recent ab initio calculations[10] show that $\theta_{1e} = 344.2^\circ$, $\theta_{2e} = 52.2^\circ$, r_e = 2.80 Å (5.29 bohr), and $\phi = 0^\circ$, i.e., a planar configuration. The

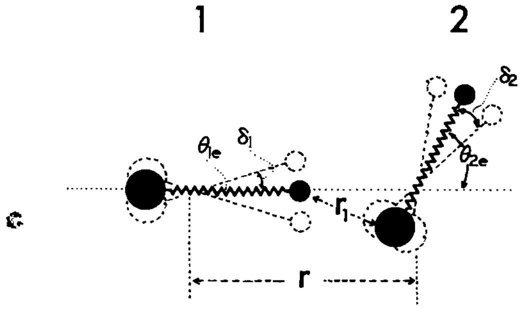

Figure 1. Near equilibrium coordinates for a hydrogen fluoride dimer. The hydrogen bond is formed between the H of molecule 1 and the F of molecule 2. The equilibrium angles are taken as $\theta_{1e} = 0°$ and $\theta_{2e} = 65°$.

dimer dissociation energy D_0 is determined as −4.63 kcal/mol. These values are in agreement with earlier ab initio SCF calculations of nonrigid dimers by Kollman and Allen,[11] Diercksen and Kraemer,[12] and Del Bene and Pople.[13] Assuming $\theta_{1e} = 0°$, Diercksen and Kraemer predict $\theta_{2e} = 60°$, the equilibrium F-F distance 2.85 Å, and $D_0 = -4.5$ kcal/mol. Del Bene and Pople give a planar equilibrium structure with $\theta_{1e} = 356°$, $\theta_{2e} = 69°$, the equilibrium F-F distance 2.55 Å, and $D_0 = -5.2$ kcal/mol. The data of the molecular beam electric resonance method by Dyke, Howard, and Klemperer[7] support the geometry of such a planar dimer with $\theta_{1e} \simeq 0°$, $\theta_{2e} = 60\text{–}70°$, and the equilibrium F-F distance 2.79 Å. The experimental hydrogen-bond dissociation energy is known[8,9] as 6.0 ± 1.5 kcal/mol. We shall take $\theta_{1e} = 0°$, $\theta_{2e} = 65°$, $r_e = 2.79$ Å, and $D_0 = -6$ kcal/mol in performing numerical analyses in what follows. Of the atom-atom interactions, the most important one for the formation of a hydrogen bond is the strong attraction between H of the first molecule (molecule 1) with F of the second molecule (molecule 2). The distance of this interaction is represented in the figure as r_1. For small displacement from the equilibrium configuration, $r \simeq r_e$, and we can approximate the distance as[5]

$$r_1 = r - q_F(d + x_1)\cos\theta_1 - q_H(d + x_2)\cos\theta_2 \tag{1}$$

where x_i is the displacement of the vibrational coordinate from the equilibrium value d and $q_{H,F} = m_{H,F}/(m_H + m_F)$. To derive eq 1 we have neglected the second and higher-order terms in (d/r). The magnitude of the second-order term can be estimated as[14] $(d/r_e)^2 = (0.917/2.80)^2 = 0.107$. Furthermore, this term is multiplied by either q_F^2 or q_H^2, so the approximation for obtaining r_1 as shown in eq 1 is reasonable. Note that $q_F = 0.950$ and $q_H = 0.050$ for HF and $q_F = 0.905$ and $q_D = 0.095$ for DF. Of course, the approximation is invalid for the perpendicular or parallel orientations, but the experimental and ab initio results show that a nonrigid dimer is not formed with such orientations.

If a rigid dimer is formed, the energy which binds two HF molecules would be the hydrogen-bond dissociation energy D_0. However, the molecules undergo slow back-and-forth translational motion about the equilibrium separation r_e and the hindered-rotational (small-amplitude oscillatory) motion around θ_{1e} and θ_{2e}, thus causing the effective strength of the hydrogen bond to decrease from D_0. A function which adequately describes such near-equilibrium behavior can then be given by

$$U(r_1) = D_0\left[\exp\left(\frac{r_{1e} - r_1}{a}\right) - 2\exp\left(\frac{r_{1e} - r_1}{2a}\right)\right] \tag{2}$$

which reduces to $-D_0$ when the dimer maintains the equilibrium configuration. Here, r_{1e} is the equilibrium value of r_1. The hydrogen-bond dissociation energy is known. Furthermore, the equilibrium values θ_{1e}, θ_{2e}, and r_e(F-F) are also known. Therefore, the interaction energy in the neighborhood of the equilibrium configuration can be readily determined as a function of the back-and-forth translational coordinate (r), the hindered-rotational coordinates (δ_1, δ_2), and the vibrational coordinates (x_1, x_2). With eq 1 the interaction energy can then be expressed as

$$\begin{aligned} U(r,\delta_1,\delta_2,x_1,x_2) = D_0 \Bigg\{ & \exp\left(\frac{r_e - r}{a}\right)\exp\Bigg[\frac{q_F x_1 \cos\theta_{1e}}{a} \\ & + \frac{q_H x_2 \cos\theta_{2e}}{a} - \frac{q_F(d + x_1)}{2a}\delta_1^2\cos\theta_{1e} \\ & - \frac{q_H(d + x_2)}{2a}(\delta_2^2\cos\theta_{2e} + 2\delta_2\sin\theta_{2e})\Bigg] \\ & - 2\exp\left(\frac{r_e - r}{2a}\right)\exp\Bigg[\frac{q_F x_1\cos\theta_{1e}}{2a} \\ & + \frac{q_H x_2\cos\theta_{2e}}{2a} - \frac{q_F(d + x_1)}{4a}\delta_1^2\cos\theta_{1e} \\ & - \frac{q_H(d + x_2)}{4a}(\delta_2^2\cos\theta_{2e} + 2\delta_2\sin\theta_{2e})\Bigg]\Bigg\} \end{aligned} \tag{3}$$

where the approximations $\cos\theta_1 \simeq \cos\theta_{1e}\cos\delta_1 \simeq \cos\theta_{1e}(1 - \delta_1^2/2)$ and $\cos\theta_2 = \cos\theta_{2e}\cos\delta_2 - \sin\theta_{2e}\sin\delta_2 \simeq \cos\theta_{2e}(1 - \delta_2^2/2) - \delta_2\sin\theta_{2e}$ were used. Note that these two approximations are different from each other because $\theta_{1e} \simeq 0°$ while $\theta_{2e} = 60\text{–}70°$ so that the sine term in the second relation cannot be neglected. If $\delta_1 = \delta_2 = 0$ and $x_1 = x_2 = 0$, eq 3 reduces to

$$U(r) = D_0\left[\exp\left(\frac{r_e - r}{a}\right) - 2\exp\left(\frac{r_e - r}{2a}\right)\right] \tag{4}$$

which describes the back-and-forth translational motion of individual molecules of the dimer near the equilibrium configuration. The configuration of a rigid dimer is maintained when $r = r_e$, $\delta_1 = \delta_2 = 0$, and $x_1 = x_2 = 0$, for which conditions eq 3 and 4 reduce to $U(r_e) = -D_0$ as it should. Equation 3 is of course not valid for molecular orientations which are significantly different from the equilibrium geometry. However, such orientations do not contribute to the formation of nonrigid dimers and are excluded from the present near-equilibrium model. As temperature increases, the molecules tend to undergo complete rotational motion, thus causing the rupture of hydrogen bonds. The present model cannot describe vibration-vibration energy transfer processes taking place at such temperatures, and the model of complete rotational motion has to be used [see eq 21].

For the near-equilibrium configuration, the deviations x_i and δ_i are small. Therefore, by expanding the δ_i- and x_i-dependent exponential factors of eq 3 in power series, we find with sufficient accuracy the potential function for the nonrigid dimer as

$$\begin{aligned} U(r,\delta_1,\delta_2,x_1,x_2) = {} & D_0\left[\exp\left(\frac{r_e - r}{a}\right) - 2\exp\left(\frac{r_e - r}{2a}\right)\right] \\ & + D_0\left[\exp\left(\frac{r_e - r}{a}\right) - \tfrac{1}{2}\exp\left(\frac{r_e - r}{2a}\right)\right]\left(\frac{q_H q_F}{a^2}\right)\cos\theta_{1e} \\ & \times \cos\theta_{2e}x_1x_2 + D_0\left[\exp\left(\frac{r_e - r}{a}\right) - \exp\left(\frac{r_e - r}{2a}\right)\right] \\ & \times\left[\frac{q_F x_1}{a}\cos\theta_{1e} + \frac{q_H x_2}{a}\cos\theta_{2e} - \frac{q_F(d + x_1)}{2a}\delta_1^2\cos\theta_{1e}\right. \\ & \left. - \frac{q_H(d + x_2)}{2a}(\delta_2^2\cos\theta_{2e} + 2\delta_2\sin\theta_{2e})\right] \\ & + \tfrac{1}{8}D_0\left[\exp\left(\frac{r_e - r}{a}\right) - \tfrac{1}{2}\exp\left(\frac{r_e - r}{2a}\right)\right]\{[q_F(d + x_1) \\ & \times \cos\theta_{1e}\delta_1^2]^2 + [q_H(d + x_2)(\delta_2^2\cos\theta_{2e} + 2\delta_2\sin\theta_{2e})]^2\} \end{aligned} \tag{5}$$

The first term of this equation determines the back-and-forth translational motion and the remaining terms the coupling of the latter motion with hindered rotational and/or vibrational motion of the molecules. Since $q_F \gg q_H$, this equation shows that the hindered rotational motion of only one molecule (molecule 1) of the nonrigid dimer is of major importance for the intermolecular coupling. This is due to the situation that the hindered rotational motion displaces the light H atom by a significant extent while the displacement of the heavy F atom is negligible. Thus, the center of mass of HF nearly coincides with that of the F atom, and molecule 1 can be readily perturbed because its H atom is in interaction with the heavy F atom of molecule 2. If the molecule is in a vibrationally excited state it can transfer the energy to its own hindered rotational motion intramolecularly. Of course, the second molecule also undergoes the hindered motion but the coupling with the first molecule occurs through the F atom which is only slightly displaced from the equilibrium angle. It should be noted that there are two equivalent configurations for the dimer, one of which is shown in Figure 1. The other form occurs when the molecules flip between two equivalent configurations in which the nonbonded and bonded hydrogen exchange roles due to quantum mechanical tunneling through a potential barrier.[15,16] However, the near-equilibrium motion of the present model cannot cause such a large-amplitude oscillation, and the transfer of vibrational energy of molecule 1 only needed to be considered. When molecule 1 is in a multiquantum state, the vibrational energy can be efficiently transferred to a near-resonant state of molecule 2 intermolecularly; e.g., HF/DF($v = 2$) + HF/DF($v = 0$) → HF/DF($v = 1$) + HF/DF($v = 1$) + ΔE, where ΔE is now removed by the restricted translational motion.

By setting $x_1 = x_2 = 0$ in eq 5, we obtain the potential energy function which is in a form suitable for the study of the hindered rotational and back-and-forth translational motion of molecules in the nonrigid dimer:

$$\begin{aligned} U(r,\delta_1,\delta_2) = {} & D_0 \left[\exp\left(\frac{r_e - r}{a}\right) - 2\exp\left(\frac{r_e - r}{2a}\right) \right] \\ & - D_0 \left[\exp\left(\frac{r_e - r}{a}\right) - \exp\left(\frac{r_e - r}{2a}\right) \right] \left[\frac{q_F d}{2a} \delta_1^2 \right. \\ & \left. \times \cos\theta_{1e} + \frac{q_H d}{2a} (\delta_2^2 \cos\theta_{2e} + 2\delta_2 \sin\theta_{2e}) \right] \\ & + \tfrac{1}{8} D_0 \left[\exp\left(\frac{r_e - r}{a}\right) - \tfrac{1}{2}\exp\left(\frac{r_e - r}{2a}\right) \right] \{(q_F d \delta_1^2 \\ & \times \cos\theta_{1e})^2 + [q_H d(\delta_2^2 \cos\theta_{2e} + 2\delta_2 \sin\theta_{2e})]^2\} \qquad (6) \end{aligned}$$

This equation cannot be used to describe the properties of the molecules which are in vibrationally excited states, but it is an important function which is needed in determining the restricted motion at the near-equilibrium configuration. It represents the coupling of the back-and-forth translational motion with the hindered rotational motion and can also be useful in studying problems such as the thermodynamic behavior of nonrigid hydrogen fluoride dimers since for eq 6 the classical partition function can be readily obtained in a rigorous form.[17,18]

Hindered Rotational Motion

At large relative separations the interaction energy is small and the molecules undergo complete rotational motion. As the molecules approach a certain distance, say r^0, they cease to be capable of performing complete rotational motion due to the formation of the hydrogen bond. Closer than this distance the molecules form a dimer and commence to oscillate, the motion being described by eq 6. When the relative separation becomes r_e, the back-and-forth translational motion as well as the oscillatory motion is arrested as expected from eq 6. We can now determine the potential function for the hindered rotational motion, which is restricted in the range $r_e < r < r^0$. Although r can be less than r_e, it would represent an unfavorable configuration since the dimer is in a compressed state. However, allowance of the oscillatory motion leads to the introduction of the effective hydrogen bond energy and the new equilibrium separation r_e^*. Then, the purely hindered-rotational motion of the molecules can be defined as

$$V(\delta_1,\delta_2) = U(r_e^*,\delta_1,\delta_2) - U(r_e^*,0,0) \qquad (7)$$

where the first term is the function given by eq 6 evaluated at $r = r_e^*$. The energy term $U(r_e^*,0,0)$ can also be obtained from eq 6 by setting $\delta_1 = \delta_2 = 0$ as well as $r = r_e^*$. Here we are interested in the hindered rotational motion of molecule 1, the potential of which can then be obtained from eq 6 and 10 by setting $\delta_2 = 0$ as

$$\begin{aligned} V(\delta_1) = {} & D_0 \left[\exp\left(\frac{r_e - r_e^*}{2a}\right) - \exp\left(\frac{r_e - r_e^*}{a}\right) \right] \\ & \times \left(\frac{q_F d}{2a}\right) \delta_1^2 \cos\theta_{1e} + \tfrac{1}{8} D_0 \left[\exp\left(\frac{r_e - r_e^*}{a}\right) \right. \\ & \left. - \tfrac{1}{2}\exp\left(\frac{r_e - r_e^*}{2a}\right) \right] \left(\frac{q_F d}{a}\right)^2 \delta_1^4 \cos\theta_{1e} \\ & \equiv K\delta_1^2 + L\delta_1^4 \qquad (8) \end{aligned}$$

The wave equation for the hindered rotational motion of molecule 1 can be written in the form

$$\frac{d^2\phi}{d\delta_1^2} + \frac{2I}{\hbar^2}[E - (K\delta_1^2 + L\delta_1^4)]\phi = 0 \qquad (9)$$

for which the approximate eigenvalues to first order are

$$E_n = (n + \tfrac{1}{2})\hbar\omega_{HR} + L\langle n|\delta_1^4|n\rangle \qquad (10)$$
$$n = 0, 1, 2, \ldots$$

where $\omega_{HR} = (2K/I)^{1/2}$, I is the moment of inertia of the molecule, and $|n>$ is the nth eigenket for the harmonic oscillator. From eq 9 and 10, the unperturbed system has the well-known solution

$$\phi_n^0 = \frac{1}{(2^n n!)^{1/2}} \left(\frac{\alpha}{4}\right)^{1/4} \exp(-\tfrac{1}{2}\alpha\delta_1^2)\, H_n(\alpha^{1/2}\delta_1) \quad (11)$$

and the eigenvalue $E_n^0 = (n + \tfrac{1}{2})\hbar\omega_{HR}$, respectively, where $\alpha = (2IK)^{1/2}/\hbar$ and H_n is the Hermite polynomial. The calculation of the perturbation term of eq 10 is simple; the result is

$$E_n = (n + \tfrac{1}{2})\hbar\omega_{HR} + \frac{3L}{4K}\frac{\hbar^2}{I}(n^2 + n + \tfrac{1}{2}) \qquad (12)$$

From the use of perturbation theory the first-order wave function for eq 8 can be obtained as

$$\begin{aligned} \psi_n = {} & \phi_n^0 + \frac{L}{4\hbar\omega_{HR}} \left(\frac{\hbar}{2I\omega_{HR}}\right)^2 \{[n(n-1)(n-2) \\ & \times (n-3)]^{1/2}\phi_{n-4}^0 + 4(2n-1)[n(n-1)]^{1/2}\phi_{n-2}^0 \\ & - 4(2n+3)[(n+1)(n+2)]^{1/2}\phi_{n+2}^0 \\ & - [(n+1)(n+2)(n+3)(n+4)]^{1/2}\phi_{n+4}^0\} \qquad (13) \end{aligned}$$

The calculated values of K and L defined in eq 8 are 22.4×10^{-14} and 3.26×10^{-14} erg for HF + HF, respectively. The frequency of the hindered-rotational motion is found to be $\nu_{HR} = \omega_{HR}/2\pi = 308\ \text{cm}^{-1}$. The eigenvalues of the hindered rotational motion can then be calculated from eq 12 and the result of the first five levels is listed in Table I. The table shows that the contribution of the perturbation term of E_n is not significant particularly for small values of n.

We shall now determine r_e^*, the new equilibrium separation

Table I. Eigenvalues of the Hindered-Rotational Motion of HF + HF

n	$(n + \frac{1}{2})\hbar\omega_{\mathrm{HR}}$	$\frac{3L\hbar^2}{4KI}(n^2 + n + \frac{1}{2})$	Sum (E_n)
0	3.06[a]	0.045	3.10
1	9.19	0.229	9.42
2	15.3	0.595	15.9
3	21.4	1.14	22.5
4	27.5	1.87	29.3
5	33.7	2.79	36.5

[a] All numbers are in units of 10^{-14} erg.

defined in eq 7. Since we are interested in the near-equilibrium behavior of the molecules in a nonrigid dimer, it is not necessary to obtain the function which is in a suitable form over wide ranges of r and θ. Obviously, the formulation of such a function would be both interesting and important, but it could only be accomplished after introducing many adjustable parameters which will obscure the real problem under consideration. Equation 3 describes then both the back-and-forth translational motion and hindered rotational motion of two molecules around the near-equilibrium geometry in the nonrigid dimer. Since the molecules are undergoing such equilibrium motion the effective strength of the hydrogen bond is not the nonrigid value D_0 but can be significantly weaker than it. In ref 5, we have determined the effective hydrogen-bond energy as

$$U(r_e^*) = D_0\left[A \exp\left(\frac{r_e - r_e^*}{a}\right) - 2B \exp\left(\frac{r_e - r_e^*}{2a}\right)\right] \equiv -D_0^* \quad (14)$$

where A and B are constants and $A \neq B \neq 1$. If $A = B = 1$, the equilibrium separation is, of course, r_e and the equilibrium hydrogen-bond energy is $U(r_e) = -D_0$. It is important to emphasize that $D_0^* < D_0$ because the hindered motion in the nonrigid dimer acts to reduce the strength of the rigid hydrogen bond D_0. At $r = r_e^*$ the hydrogen bond takes the energy D_0^* and the incident molecules with $E \leq D_0^*$ will be trapped in the attractive well forming a nonrigid dimer. Therefore, the hindered rotational potential energy should be evaluated at r_e^* as given by eq 7. With the potential constants given above, we find $D_0^* = 21.5 \times 10^{-14}$ erg with $|r_e - r_e^*| = 0.232$ Å from eq 14 for HF + HF. For DF + DF, $|r_e - r_e^*| = 0.193$ Å and $D_0^* = 18.7 \times 10^{-14}$ erg, when the equilibrium orientation angles are assumed to be the same as those of HF + HF.

When we wish to investigate transitions among the hindered rotational states, it is necessary to calculate the matrix element $I_{n'n} = \langle n'|\delta_1{}^2|n\rangle$, where the anharmonic wave functions $(\psi_n, \psi_{n'})$ are linear combinations of the harmonic functions as given by eq 13, so the matrix element is a sum of the harmonic terms each of which satisfies the selection rule $\Delta n = \pm 2$. When the hydrogen fluoride molecules collide (one of which is in the vibrationally excited state, say $v = 1$, and the other in the ground state) they can form a loosely bound complex for the relative separation less than r^0 and the vibrational energy would be transferred to the hindered motion, i.e., HF/DF($v = 1$) + HF/DF($v = 0$) → HF/DF($v = 0$) + HF/DF($v = 0$). The hindered motion can gain the energy $|n - n'|\hbar\omega_{\mathrm{HR}}$ and the energy mismatch $\hbar\omega - |n - n'|\hbar\omega_{\mathrm{HR}} = \Delta E'$ would transfer to the back-and-forth translational motion. On the other hand, when a vibration-vibration process such as HF/DF($v = 2$) + HF/DF($v = 0$) → HF/DF($v = 1$) + HF/DF($v = 1$) + ΔE is taking place, the energy mismatch can be small such that $|\Delta E| < 2\hbar\omega_{\mathrm{HR}}$. For such a case, the hindered motion cannot then remove the energy ΔE; instead, it can be transferred to the back-and-forth translational motion. The latter process is simple to handle in the present model since it does not involve energy transfer to the hindered motion in which case the energy can partition into all possible hindered states. In what follows, we shall apply the idea of nonrigid dimer formation to the vibration-vibration energy transfer in hydrogen fluorides. First, the near-resonant process DF($v = n$) + DF($v = 0$) at low temperatures will be discussed in the next section. We shall also discuss the importance of the complete rotational motion of colliding molecules. The dimer model will then be applied to the self-deexcitation process DF($v = 1$) + DF($v = 0$) → DF($v = 0$) + DF($v = 0$).

Vibrational Deexcitation of DF(n) by DF(0)

We now consider the intermolecular vibration-vibration energy transfer process DF($v = n$) + DF($v = 0$) → DF($v = n - 1$) + DF($v = 1$) for n = 2, 3, 4, and 5. Since the magnitudes of ΔE for these processes are small, the hindered rotational motion cannot participate to remove the energy mismatch for DF($v = n$); instead ΔE can be taken away by the back-and-forth translational motion of the molecules in nonrigid dimers. Then, the perturbation energy which is responsible for such deexcitation processes is the second term of eq 5, namely,

$$V'(r,x_1x_2) = D_0 \cos\theta_{1e} \cos\theta_{2e}\left(\frac{q_{\mathrm{H}}q_{\mathrm{F}}}{a^2}\right) \times \left[\exp\left(\frac{r_e - r}{a}\right) - \tfrac{1}{2}\exp\left(\frac{r_e - r}{2a}\right)\right] x_1x_2 \quad (15)$$

In nonrigid dimers, the translational motion is restricted to the neighborhood of r_e, so the exponential terms in eq 15 can be expanded for $r \simeq r_e$, and we retain the term containing $(r_e - r)$:

$$V'(r,x_1x_2) = \tfrac{3}{2} D_0 \cos\theta_{1e} \cos\theta_{2e} \times \left(\frac{q_{\mathrm{H}}q_{\mathrm{F}}}{a^2}\right)\left(\frac{r_e - r}{2a}\right) x_1x_2 \quad (16)$$

The probability of the deexcitation DF($v = n$) + DF($v = 0$) → DF($v = n - 1$) + DF($v = 1$) to first order of perturbation theory is[19]

$$P_{n,0}{}^{n-1,1} = \hbar^{-2}\left|\langle n - 1,1|\int_{-\infty}^{\infty} V'[r(t),x_1x_2] \times \exp(i\Delta Et/\hbar)\, \mathrm{d}t\,|n,0\rangle\right|^2 \quad (17)$$

In ref 5, we have derived the trajectory for the back-and-forth translational motion as

$$\left(\frac{r_e - r}{2a}\right) = (E/D_0)^{1/2} \cos[(D_0/2\mu)^{1/2}(t/a)] \quad (18)$$

where E is the initial relative energy with respect to the minimum in the dimer attractive well and μ is the reduced mass. For HF + HF, with the assumed value[5] $a = 0.2$ Å, we find that the period of the back-and-forth motion is 1.12×10^{-13} s. The motion which is described by the cosine function in eq 18 repeats many times in the dimer during the collision process. For $E/D_0 = 0.5$, the extreme value of $|r_e - r|/2a$ is 0.707, so the extension and compression of the hydrogen bond is +0.283 or −0.283 Å. For the low energy motion of $E/D_0 = 0.1$, the extreme value is only 0.126 Å. Note that the equilibrium F–F distance is known to be 2.79 Å.[7]

From eq 16 and 18, the integral in eq 17 can be evaluated as[20]

$$\int_{-\infty}^{\infty} D_0\left(\frac{r_e - r}{2a}\right)\exp\left(\frac{i\Delta Et}{\hbar}\right)\mathrm{d}t = \frac{a\pi(2\mu E)^{1/2}}{4B\left(\frac{3+s}{2}, \frac{3-s}{2}\right)} \quad (19)$$

where B is the β function with $s = (a\Delta E/\hbar)(2\mu/D_0)^{1/2}$.

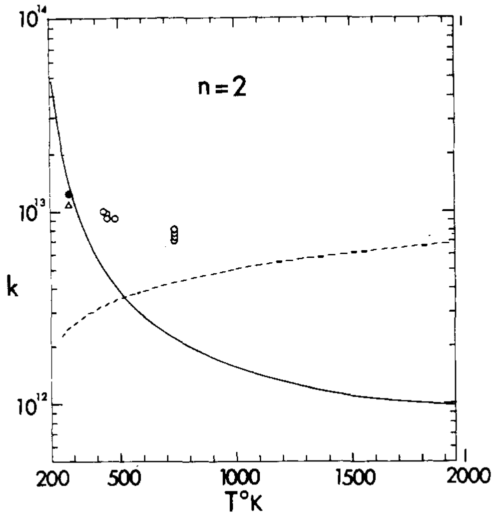

Figure 2. Temperature dependence of rate coefficients for DF(v = 2) + DF(v = 0) → DF(v = 1) + DF(v = 1). The solid curve represents the result of the nonrigid dimer model, eq 20, the broken curve represents the result of the rotational model, eq 21, and the dotted curve represents the sum of these two results. Experimental data: (●) ref 25, (○) ref 26, (△) ref 27. Rate coefficients are expressed in units of $cm^3/(mol\ s)$.

Equation 18 indicates that the displacement $(r_e - r)$ of the molecule in the dimer is maximum at $t = 0$ and zero at $t = \pm\tau/4$, where τ is the period of the back-and-forth motion defined as $\tau = 2\pi(\mu/f)^{1/2} = 2\pi a(2\mu/D_0)^{1/2}$. Therefore, the displacement, which is an even function of time, changes from zero at $t = -\tau/4$ to a maximum value of $(E/D_0)^{1/2}$ at $t = 0$ and returns to zero at $t = \tau/4$. As shown by eq 18, the oscillatory motion continues as t increases. During the time interval of $t = -\tau/4$ to $\tau/4$, the energy ΔE, which is very small compared to the vibrational quantum of DF itself, can be efficiently removed by the back-and-forth translational motion. To obtain eq 19, we have set $(D_0/2\mu)^{1/2}(t/a) = x$ and the integration limits are taken as $x = -\pi/2$ and $\pi/2$. This interval corresponds to $t = -\tau/4$ and $\tau/4$, respectively.

From eq 17 and 19, the thermal-average transition probability can then be obtained as

$$P_{n,0}{}^{n-1,1}(T) = (kT)^{-1} \times \int_0^{D_0^*} P_{n,0}{}^{n-1,n}(E) \exp[-(E - D_0^*)/kT]\, dE$$

$$= 2\mu \left(\frac{3\pi q_H q_F}{16M\omega a}\right)^2 \left[\frac{\cos\theta_{1e}\cos\theta_{2e}}{B\left(\frac{3+s}{2}, \frac{3-s}{2}\right)}\right]^2 \times [\langle n-1,1|(\mathbf{a}_1{}^\dagger + \mathbf{a}_1)(\mathbf{a}_2{}^\dagger + \mathbf{a}_2)|n,0\rangle]^2[(kT + \Delta E/2)\exp(D_0^*/kT) - (D_0^* + kT + \Delta E/2)] \quad (20)$$

where $\Delta E/2$ is due to the symmetrization of the initial and final energies of the translational motion, i.e., the replacement of E by the average energy $(E + \Delta E/2)$. In this equation, $\mathbf{a}_i{}^\dagger$ and $\mathbf{a}_i$ are the phonon creation and annihilation operators, respectively. They are related to the vibrational coordinate as $x_i = (\hbar/2M\omega)^{1/2}(\mathbf{a}_i{}^\dagger + \mathbf{a}_i)$.

For DF + DF we shall take D_0 = 6 kcal/mol (41.7×10^{-14} erg), d = 0.917 Å, and $\nu = \omega/2\pi$ = 2998 cm^{-1}.[14] The value of a is assumed as 0.2 Å, but the probability given by eq 20 is not sensitive to small changes in the value. The values of the energy mismatch in wavenumbers are 91, 182, 269, and 354 cm^{-1} for n = 2, 3, 4, and 5, respectively. The effective hydrogen-bond energy calculated from eq 14 is 18×10^{-14} erg. There are no experimental data available for the equilibrium orientation angles θ_{1e} and θ_{2e}. We shall assume them by the values for HF + HF, which are known as $\theta_{1e} \simeq 0°$ and $\theta_{2e} \simeq 65°$. Although this assumption introduces an uncertainty into the calculation, the result cannot be serious since it only affects the constant term $(\cos\theta_{1e}\cos\theta_{2e})^2$. To calculate the vibrational matrix element in eq 20, we shall use the anharmonic wavefunctions which have been given in ref 5 for the anharmonic potential $V(x) = \frac{1}{2} M\omega^2(x - x_e)^2 + \beta(x - x_e)^3$. By expanding the Morse function $V(x) = D_e\{1 - \exp[-b(x - x_e)]\}^2$, we find $\beta = -D_e b^3$, where D_e and b are intramolecular potential constants. We use[21] D_e = 141 kcal/mol and b = 2.232 $Å^{-1}$ to calculate β. For n = 2, 3, 4, and 5, the anharmonic vibrational matrix element takes the values of 1.69, 2.51, 3.83, and 5.94, respectively. Since the values of the matrix element calculated with the harmonic oscillator wave functions are $2^{1/2}$, $3^{1/2}$, $4^{1/2}$, and $5^{1/2}$, the anharmonicity appears to make an important contribution to the energy transfer processes, in particularly those involving higher vibrational states. By use of the simple kinetic theory, the transition probability can be converted to the rate coefficient k; we shall express the latter quantity in units of $cm^3/(mol\ s)$. When appropriate molecular constants are used, along with the collision diameter approximated as 2.79 Å,[7] we find $k = 9.33 \times 10^{12} T^{1/2} P_{n,0}{}^{n-1,1}(T)$ $cm^3/(mol\ s)$.

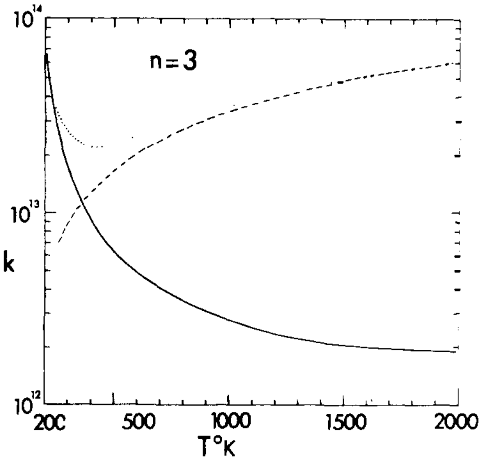

Figure 3. Temperature dependence of rate coefficients for DF(v = 3) + DF(v = 0) → DF(v = 2) + DF(v = 1). The solid curve represents the result of the nonrigid dimer model, the broken curve represents the rotational model, and the dotted curve represents the sum. Rate coefficients are expressed in units of $cm^3/(mol\ s)$.

The calculated values of k for n = 2, 3, 4, and 5 are plotted in Figures 2–5, respectively, as a function of temperature. The curves show a strong negative temperature dependence of energy transfer rates at low temperatures, reflecting the situation that the presence of strong attractive forces between molecules to form nonrigid dimers becomes less important as the temperature is raised. In eq 20 the factor $[(kT + \Delta E/2)\exp(D_0^*/kT) - (D_0^* + kT + \Delta E/2)]$ stands for this "thermal" effect, and decreases with rising temperature because of the factor $\exp(D_0^*/kT)$.

Because of the nature of the model discussed above for nonrigid dimers, eq 20 cannot be expected to describe the energy transfer processes at temperatures significantly higher than 300 K. At such temperatures, the major portion of molecules is expected to undergo complete rotational motion so that the energy mismatch ΔE can be efficiently transferred to the rotational motion of the molecules. There can be a contribution coming from the nonrigid dimers which still exists at such temperatures, but it cannot be important. In fact, as shown by the solid curves in Figures 2–5, the nonrigid dimer gives very small values of k. Since at a given temperature both nonrigid dimers and rotation molecules can contribute to energy transfer, we should expect the sum of the rate coefficients

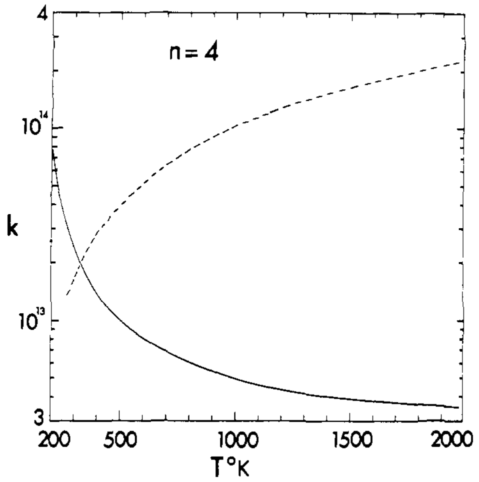

Figure 4. Temperature dependence of rate coefficients for DF(v =4) + DF(v = 0) → DF(v = 3) + DF(v = 1). The solid curve represents the result of the nonrigid dimer model, the broken curve represents the rotational model, and the dotted curve represents the sum. Rate coefficients are expressed in units of cm^3/(mol s).

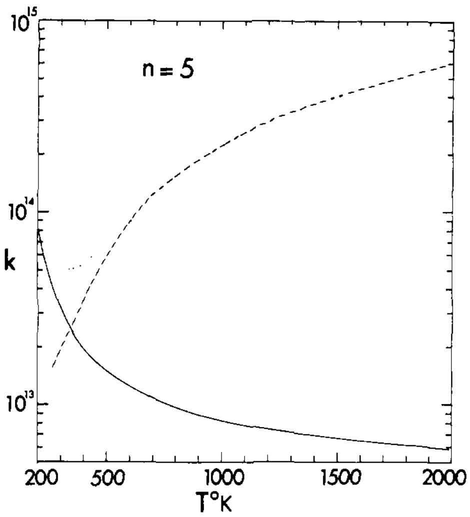

Figure 5. Temperature dependence of rate coefficients for DF(v = 5) + DF(v = 0) → DF(v = 4) + DF(v = 1). The solid curve represents the result of the nonrigid dimer model, the broken curve represents the rotational model, and the dotted curve represents the sum. Rate coefficients are expressed in units of cm^3/(mol s).

for these two types of energy transfer mechanism to describe the overall process. At low temperatures the vibration–vibration energy transfer through the formation of nonrigid dimers is important, while at high temperatures the energy transfer through the complete rotational motion of the colliding molecules essentially describes the overall process. When the molecule undergoes complete rotational motion, the vibrational energy mismatch ΔE of the vibration–vibration process can be efficiently transferred to the rotational motion of molecule 2 intermolecularly. The energy transfer rate coefficient may be calculated from the vibration–vibration–rotation probability derived elsewhere:[22,23]

$$P_{n,0}{}^{n-1,1}(T) = 4\left(\frac{\pi\phi_1\Delta E}{\hbar\omega}\right)^2$$
$$\times\,[\langle n-1,n|(\mathbf{a}_1{}^\dagger+\mathbf{a}_1)(\mathbf{a}_2{}^\dagger+\mathbf{a}_2)|n,0\rangle]^2 f_{\mathrm{VT}}$$
$$\times\left[1-\frac{\hbar}{2(1+\gamma)\Delta E}\left(\frac{Dq_{\mathrm{F}}}{a'dM}\right)^{1/2}\frac{\phi_2}{\phi_1}\right]^2$$
$$\times\int_0^\infty \exp[-f(E)-E/kT]\,(\mathrm{d}E/kT) \qquad (21)$$

where

$$\phi_1 = \frac{\cosh Q_2+\cosh Q_1}{\sinh Q_2+(Q_2/Q_1)\sinh Q_2}-\frac{1}{Q_2}$$

$$Q_{1,2} = q_{\mathrm{H,F}}d/a'$$

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

$$f(E) = \frac{(2I)^{1/2}\pi\gamma_0\Delta E}{\hbar E^{1/2}}-\frac{2(2ID)^{1/2}\gamma_0\Delta E}{\hbar E}g$$

$$\gamma = \frac{9}{2Q_2{}^2}\left(1+\frac{4}{3Q_2{}^2}\right)$$

$$\gamma_0 = (1+\gamma)a'/q_{\mathrm{F}}d$$

Here D is the attractive energy between two colliding molecules and is taken as 400 K.[22] The potential parameter a' in the rotational model is weakly temperature dependent; the values change from 0.202 Å at 300 K to 0.183 Å at 2000 K.[22] When the matrix element takes the harmonic oscillator value of $2^{1/2}$ for $n = 2$ and the E integral is explicitly evaluated as[24]

$$I_E = \int_0^\infty \exp[-f(E)-E/kT]\,(\mathrm{d}E/kT)$$
$$\simeq \left(\frac{4\pi}{3}\right)^{1/2}\left(\frac{\chi}{kT}\right)^{1/2}\left[1-\frac{8g}{3\pi}\left(\frac{D}{\chi}\right)^{1/2}\right]^{5/4}$$
$$\times\exp\left[-\frac{3\chi}{kT}+\frac{4(D\chi)^{1/2}}{\pi kT}g+\frac{16D}{3\pi^2kT}g^2-\frac{\Delta E}{2kT}\right] \qquad (22)$$

we find the expression of the probability given in ref 23 excluding the factor representing hydrogen-bond and dipole-dipole interactions. Here,

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

$$\chi = \left[\left(\frac{M}{2q_{\mathrm{F}}}\right)^{1/2}\pi(1+\gamma)\left(\frac{\Delta E}{\hbar}\right)a'kT\right]^{2/3}$$

The rotational motion of DF is accompanied by the relative translational motion, which takes away a part of the energy mismatch. The factor f_{VT} in eq 21 represents this effect and takes the form

$$f_{\mathrm{VT}} = 1-2(K'-K'^2)(1+\Delta E/2kT)+K'^2(\Delta E/2kT)^2$$

where $K' = t^*kT/\omega\mu a'^2$, $t^* = \pi(I/2E^*)^{1/2}\gamma_0[1-(2\pi)(D/E^*)^{1/2}g]$, and $E^* = \chi-(8g/3\pi)(D\chi)^{1/2}$. If the molecules were assumed to be "frozen" at a certain distance and then transfer vibrational energy to the rotational motion, this factor would be unity. The magnitude of this factor increases with temperature since the translational motion becomes important at higher temperatures.

For the present VV processes the coefficients of $E^{-1/2}$ and E^{-1} defined in $f(E)$ are small because of the term ΔE, so the integrand of eq 22 is a slowly varying function of E. For such a case, the right-hand side of eq 22 is less reliable since the method described in ref 23 becomes inaccurate; therefore we have integrated I_E on a computer using Simpson's rule. Since the average energy is $E - \Delta E/2$ for the endothermic process, the energy E in $f(E)$ is replaced by this energy and I_E is integrated from $E = \Delta E$ to ∞. The result for each deexcitation process is in Figures 2-5. Below room temperature, the rate coefficient obtained from eq 21 is very small compared with the dimer result and increases with temperature. The increase is slow for $n = 2$ but becomes quite fast as n increases over the entire temperature range under consideration. For $n = 2$, the nonrigid dimer model gives very large values of the rate coefficient below 500 K. Above this temperature, on the other hand, the rotational model gives large values of k, but the values increase slowly with temperature. The sum of these two deexcitation rate coefficients, therefore, decreases sharply with rising temperature and then increases slowly at higher temperatures. The agreement between the sum and the experimental data[25-27] is good. The sum of two models is plotted in Figure 6 for n = 2-5. For higher values of n, a similar trend in the sum is seen with the exception that the rotational model gives larger values of k compared to the dimer model and that the minimum values occur at lower temperatures. The latter situation leads to the appearance of the negative temperature dependence below room temperature. For $n > 2$, no experimental data are available, so the test of the prediction given in Figure 6 cannot be made.

Self-Deexcitation Probability of Hydrogen Fluorides

In this section we shall apply the dimer model to the self-deexcitation process DF($v = 1$) + DF($v = 0$) → DF($v = 0$) + DF($v = 0$) at low temperatures (<300 K). In this process ΔE is so large (2907 cm^{-1}) that the slow back-and-forth translational motion alone cannot remove all the energy. Unlike the near-resonant process treated in the previous section, we now have to consider the participation of the hindered rotational motion in the deexcitation process. Therefore, the perturbation potential function which is appropriate for the study of this process must show the coupling of the vibrational motion (x_1) with the back-and-forth motion (r) and the hindered rotational motion (δ_1). The hindered motion of molecule 2 (i.e., δ_2) is not important since its coupling with the vibrational motion of molecule 1 is through the F atom, which undergoes only a very small displacement around θ_{2e}. The energy ΔE is thus considered to transfer to the oscillatory motion of molecule 1 intramolecularly and to the back-and-forth motion intermolecularly. The perturbation energy for the coupling between these three types of motion is obtained from eq 5 as

$$V'(r,x_1,\delta_1) = -D_0\left[\exp\left(\frac{r_e - r}{a}\right) - \exp\left(\frac{r_e - r}{2a}\right)\right]\left(\frac{q_F\cos\theta_{1e}}{2a}\right)x_1\delta_1^2 \simeq -D_0\left(\frac{r_e - r}{2a}\right)\left(\frac{q_F\cos\theta_{1e}}{2a}\right)x_1\delta_1^2 \quad (23)$$

As shown in eq 5, there is a term containing the factor $x_2\delta_2^2$ of molecule 2, but this term stands for the intramolecular energy transfer between the vibrational motion and hindered rotational motion of molecule 2. Since the vibrational state of molecule 2 remains unchanged during the self-deexcitation process, this term does not contribute to the perturbation energy derived above. It should also be noted that this term contains q_H, which is very small compared to q_F for DF + DF. In eq 5, there is a term containing $(d + x_1)^2\delta_1^4$, but this term is negligible compared to that given by eq 23.

The energy transfer probability can be obtained as in eq 17 as

$$P_{10,n}{}^{00,n'} = \hbar^{-2}\left[\langle 00,n'|\int_{-\infty}^{\infty} V'(r,x_1,\delta_1) \times \exp(i\Delta Et/\hbar)\,\mathrm{d}t\,|10,n\rangle\right]^2 \quad (24)$$

which, with eq 23, takes the form

$$P_{10,n}{}^{00,n'} = \frac{1}{(a\hbar)^2}\left[\int_{-\infty}^{\infty} D_0\left(\frac{r_e - r}{2a}\right)\exp\left(\frac{i\Delta Et}{\hbar}\right)\mathrm{d}t\right]^2 \times [\langle 0|x_1|1\rangle]^2\left[\frac{q_F\cos\theta_{1e}}{2}\langle n'|\delta_1^2|n\rangle\right]^2 \quad (25)$$

With the result given by eq 19, $\langle 0|x_1|1\rangle = (\hbar/2M\omega)^{1/2}$, and the evaluation of the hindered rotational matrix element with respect to $\phi_n{}^0$ as

$$\langle n'|\delta_1^2|n\rangle = [(n + 1)(n + 2)]^{1/2}/2\alpha \quad (26)$$

$$n' = n + 2$$

we find

$$P_{10,n}{}^{00,n+2}(E) = \left[\frac{\pi}{4B\left(\frac{3+s}{2},\frac{3-s}{2}\right)}\right]^2\left(\frac{\mu}{M\hbar\omega}\right)\left\{\left[\frac{\hbar q_F\cos\theta_{1e}}{4(2IK)^{1/2}}\right]^2 \times (n + 1)(n + 2)\right\}E \quad (27)$$

where the quantity in the curled brackets represents the hindered rotational transition $n \rightarrow n + 2$. Since many transitions of the type $n \rightarrow n + 2$ are possible, the final form of the thermal average probability can be expressed as

$$P_{10}{}^{00}(T) = Z_{HR}{}^{-1}\sum_n \exp(-n\hbar\omega_{HR}/kT) \times \int_0^{D_0^*} P_{10,n}{}^{00,n+2}(E)\exp[-(E - D_0^*)/kT](\mathrm{d}E/kT) = \left[\frac{\pi}{4B\left(\frac{3+s}{2},\frac{3-s}{2}\right)}\right]^2\left(\frac{\mu}{M\hbar\omega}\right) \times [(kT + \Delta E'/2)\exp(D_0^*/kT) - (D_0^* + kT + \Delta E'/2)][(\hbar q_F\cos\theta_{1e})^2/32IKZ_{HR}] \times \sum_n (n + 1)(n + 2)\exp(-n\hbar\omega_{HR}/kT) \quad (28)$$

where Z_{HR} is the partition function for the hindered rotational motion, $[1 - \exp(-\hbar\omega_{HR}/kT)]^{-1}$, and $\Delta E'$ is the part of ΔE that is transferred to the back-and-forth translational motion. As indicated in eq 26, transitions between hindered rotational states proceed through two-quantum processes. Since ΔE is large, transitions such as $n \rightarrow n + 2$, $n \rightarrow n + 4$, $n \rightarrow n + 6$, . . . , $n \rightarrow n + 2j$ with j = 1, 2, 3, . . . , can occur, but processes involving large values of j areinefficient. In higher-order perturbation approaches, the hindered rotational transition probability can be approximated as[28]

$$\left[\frac{q_F\cos\theta_{1e}}{2}\langle n + 2j|\delta_1^2|n\rangle\right]^2 = \frac{j!}{n![(j - n)!]^2}\left[\left(\frac{q_F\cos\theta_{1e}}{2}\right)^2\langle 2|\delta_1^2|0\rangle^2\right]^{j-n} \quad (29)$$

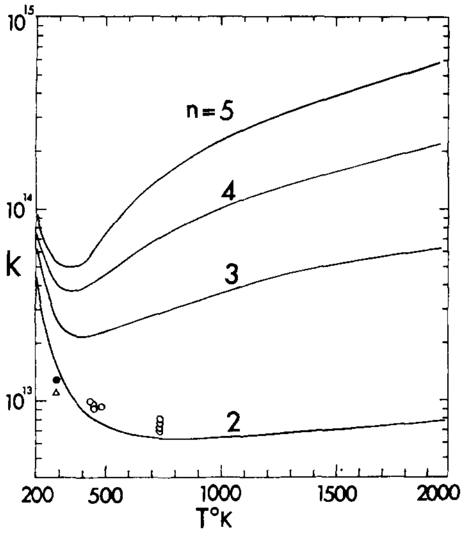

Figure 6. Temperature dependence of the sum of the rate coefficients of the nonrigid dimer and rotational models for $n = 2$–5. Experimental data: (●) ref 25, (○) ref 26, (△) ref 27. Rate coefficients are expressed in units of $\mathrm{cm}^3/(\mathrm{mol\ s})$.

where the left-hand-side is the hindered rotational matrix element given by eq 25. Numerical analyses show that $n \rightarrow n + 4$ (i.e., $j = 2$) is most important in removing the vibrational energy of DF($v = 1$). For the self-deexcitation process the amount of vibrational energy transferred to the hindered rotational motion is $4\hbar\omega_{\mathrm{HR}}$, the remaining energy $\Delta E' = \Delta E - 4\hbar\omega_{\mathrm{HR}}$ being taken away by the back-and-forth translational motion. For the self-deexcitation process $\Delta E = 57.7 \times 10^{-14}$ erg, whereas the hindered rotational quantum is only $\hbar\omega_{\mathrm{HR}} = 4.23 \times 10^{-14}$ erg. At 300 K, the first five terms of the n sum have to be included in the calculation of eq 28; at 150 K, the first three terms only are of importance. At 300 K, we find the probability $P_{10}{}^{00}(t) = 2.3 \times 10^{-3}$ but it increases to 4.1×10^{-3} at 200 K. These two values are in reasonable agreement with the recent experimental data 2.6×10^{-3} and 5.6×10^{-3}, respectively, by Lucht and Cool.[29] At 150 K no experimental data are available but the extrapolation of the data to this temperature suggests that the value would be about 1.2×10^{-2}; the calculated value from eq 28 and 29, including the first three terms of the n sums, is 1.4×10^{-2}. It is particularly interesting to note that eq 28 gives such a strong negative temperature dependence of $P_{10}{}^{00}(T)$ below 300 K. At temperatures above 300 K, the dimer model, which is based on small-amplitude oscillatory motion, may no longer be used to describe the self-deexcitation process.

Concluding Comments

A nonrigid planar dimer model is developed for hydrogen-bonded systems to describe their near-equilibrium behavior. The hydrogen bond energy for a nonrigid dimer in its near-equilibrium configuration is obtained showing its dependence on the vibrational coordinate and hindered rotational angle of each molecule of the dimer and the relative separation between the two molecules of the dimer. The hindered rotational motion is considered to be quantized, and corresponding wave functions and eigenvalues are calculated with perturbation theory. The restricted back-and-forth translational motion is treated classically and the equation of motion is solved to obtain the trajectory in a cosine function.

Application of the nonrigid dimer model is made to calculate vibrational energy transfer probabilities of DF($v = n$) + DF($v = 0$) $\rightarrow$ DF($v = n - 1$) + DF($v = 1$). For these near-resonant processes, the energy mismatch ΔE is very small and is assumed to be transferred to the restricted back-and-forth translational motion. For the self-deexcitation process DF($v = 1$) + DF($v = 0$) $\rightarrow$ DF($v = 0$) + DF($v = 0$), the energy mismatch is very large and is considered to be partitioned among the back-and-forth translational motion and the hindered rotational motion. The calculation shows that energy transfer probabilities are very large and have a strong negative temperature dependence at low temperatures.

The model is admittedly a simplified one but contains the essential features of hydroben-bonded systems near the equilibrium configuration. It has the advantage of conceptual and mathematical simplicity and gives the result which does seem to correspond to the observed data on the vibrational relaxation of deuterated hydrogen fluorides at low temperatures. The result of this approach is suggestive and the model can be extended to study the problems of dimers in which the molecules undergo large displacements from the equilibrium configuration and out-of-plane hindered rotation.

References and Notes

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(24) The function $\exp[-f(E)]$ increases with E, while the Boltzmann factor $\exp(-E/kT)$ decreases. Therefore, the integrand of I_E takes a maximum value at some intermediate energy, say E^*, which is the root of $f'(E) = 0$. Then, the integral can be evaluated as $I_E \simeq [2\pi/f''(E^*)]^{1/2} \exp[-f(E^*)]$, where $f''(E^*)$ is the second derivative of $f(E)$ evaluated at $E = E^*$. Equation 22 is the result of such an evaluation.
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