

## HF와 Ar 衝突中の 振動一回轉遷移\*

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## Simultaneous Vibrational and Rotational Transitions in HF + Ar\*

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**要約.** HF의 振動的 1→0 遷移過程에 回轉運動이 重要な 影響을 미친다는 問題를 半古典的 三次元方法으로 研究하였다. HF의 振動 energy의 大部分이 回轉運動으로 移轉되는 것을 理論적으로 詳細히 計算하였다. 振動 energy가 並進運動으로 移轉한다는 從來의 理論으로는 HF의 振動的 relaxation 過程을 說明할 수 없음을 指摘하였다.

**Abstract.** The importance of rotational transitions in the vibrational deexcitation of HF(1→0) in HF+Ar collisions has been investigated by a semiclassical three-dimensional approach. Because of the inclusion of rotational transitions, this study gives vibrational transition probabilities which are very large compared to results of conventional vibration-to-translation energy transfer theories. Currently available experimental studies suggest that this effect is important and has to be included in rigorous calculations.

### 1. Introduction

Recent experimental studies show that the self-deactivation of hydrogen halides(HX-HX) cannot be explained by a simple vibration-to-translation(VT) energy transfer mechanism.<sup>1</sup> Conventional VT energy transfer theories<sup>2</sup> give vibrational relaxation times which are several orders of magnitude longer than those of experiment. Both experimental<sup>1</sup> and theoretical<sup>3</sup> studies support that the mechanism of vibration-

to-rotation(VR) energy transfer is the dominant process in such collision systems. Although there are not enough experimental data available,<sup>1c</sup> indications are that the deexcitation of HF( $v=1$ ) by Ar is similarly much faster than those predicted by VT energy transfer theories. In such a collision system, the VT theory treats the deexcitation process as the removal of the vibrational quantum  $\hbar\omega$  by the translational motion. However, in the deexcitation(or excitation) of molecules such as HF, the coupling between rotation and vibration is usually strong so that the rotational changes accompany the vibrational transitions. Therefore, the problem of simultaneous vibrational and

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rotational transitions is both interesting and important.

It is the purpose of this paper to show the importance of rotational transitions in the deexcitation of HF ( $v=1$ ) which is in interaction with Ar. Consideration of rotational transitions requires the summing of the simultaneous probabilities over all possible rotational states in  $\bar{v}$  deriving the thermal average probability. We shall use the semiclassical theory which was developed by Lawley and Ross<sup>4</sup> and recently extended by Sørensen<sup>5</sup> for the formulation of the simultaneous transition probabilities. By solving the classical equation of motion, the transition probabilities will be obtained in explicit forms. In sec. 2, the interaction potentials are derived in appropriate forms for the study. The explicit expression of the deexcitation probability is obtained in sec. 3, and the calculation is presented in sec. 4. Although the importance of intermultiplet transitions was noted in ref. 5, we shall not include it here. Furthermore, it is not intended to investigate the temperature dependence of the probability in the present paper; rather we study the importance of individual rotational transitions on the overall deexcitation process. We shall therefore carry out calculations at one temperature, namely 300 °K.

## 2. Perturbation Potential

The potential energy which determines the relative motion of the collision system is expressed by the Morse-type function

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

where  $r$  is the relative separation of the colliding partners. To derive the perturbation energy which is responsible for the vibrational and rotational transitions we start with the sum of two atom-atom interactions:

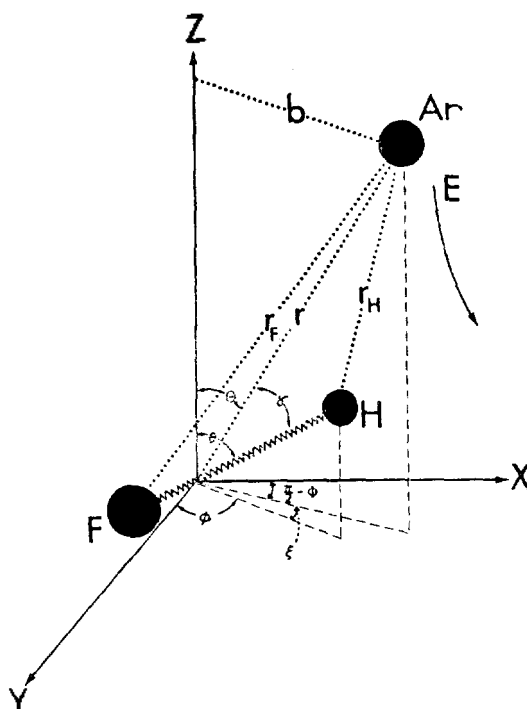


Fig. 1. Geometry of the collision of HF with Ar in the center-of-mass system with the molecule fixed at the origin and the Z axis aligned with the incident direction of Ar. The spherical angles of the axis of HF are  $\theta$  and  $\phi$ . The direction of Ar is given by the angles  $\theta$  and  $\phi$ .

$$U(r_H, r_F) = D \left\{ \exp\left(l - \frac{r_H}{a}\right) + \exp\left(l - \frac{r_F}{a}\right) - 2 \left[ \exp\left(\frac{l}{2} - \frac{r_H}{2a}\right) + \exp\left(\frac{l}{2} - \frac{r_F}{2a}\right) \right] \right\} \quad (2)$$

where  $r_H, r_F$  represent, respectively, the Ar-H and Ar-F distances; see Fig. 1. At the relative separation  $r$  greater than the equilibrium bond distance  $d_0$ , we can approximate these two atom-atom distances by  $r_{H,F} = r + \rho_{H,F}(d_0 + x) \cos \gamma$ , where  $\rho_{H,F} = m_{H,F} / (m_H + m_F)$ ,  $x$  is the displacement of the bond distance from its equilibrium value, and  $\gamma$  is the angular coordinate defined in Fig. 1. When these distances are substituted in Eq. (2), we find

$$U(r, x, \gamma) = D \exp\left(l - \frac{r}{a}\right) \left[ \exp\left(\frac{\rho_F d}{a} \cos \gamma\right) \right]$$

$$\begin{aligned} & + \exp\left(-\frac{\rho_H d}{a} \cos \gamma\right) \Big] - 2D \exp\left(\frac{l}{2} - \frac{r}{2a}\right) \\ & \left[ \exp\left(-\frac{\rho_F d}{2a} \cos \gamma\right) + \exp\left(-\frac{\rho_H d}{2a} \cos \gamma\right) \right] \end{aligned} \quad (3)$$

where  $d = d_0 + x$ . The perturbation potential obtained in the first order of the vibrational amplitude is then  $(\partial U / \partial x)_{x=0}$ ; i. e.,  $-(\partial U / \partial x)_{x=0}$  is the angle-dependent perturbing force  $\mathcal{F}(r, \gamma)$ . The potential derivative evaluated  $x=0$  is

$$\begin{aligned} \left(\frac{\partial U}{\partial x}\right)_{x=0} &= D \exp\left(l - \frac{r}{a}\right) \left[ -\frac{\rho_F}{a} \exp\left(-\frac{\rho_F d_0}{a} \cos \gamma\right) \right. \\ & \quad \left. - \frac{\rho_H}{a} \exp\left(-\frac{\rho_H d_0}{a} \cos \gamma\right) \right] \cos \gamma \\ & - D \exp\left(\frac{l}{2} - \frac{r}{2a}\right) \left[ -\frac{\rho_F}{a} \exp\left(-\frac{\rho_F d_0}{2a} \cos \gamma\right) \right. \\ & \quad \left. - \frac{\rho_H}{a} \exp\left(-\frac{\rho_H d_0}{2a} \cos \gamma\right) \right] \cos \gamma. \end{aligned} \quad (4)$$

Numerically,  $\rho_F = 0.95$  and  $\rho_H = 0.05$  so the exponential factors which are due to the Ar-F interaction can be linearized. On the other hand, the factors representing the Ar-H interaction are very large and cannot be linearized; we express them in a polynomial form

$$\begin{aligned} \exp\left(-\frac{\rho_F d_0}{a} \cos \gamma\right) &= \left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}} \sum_{n=0}^{\infty} (2n+1) I_{n+1/2} \\ & \quad (\alpha) P_n(\cos \gamma), \end{aligned} \quad (5)$$

where  $\alpha = \rho_F d_0 / a$ ,  $I_{n+1/2}(\alpha)$  are the modified Bessel functions, and  $P_n(\cos \gamma)$  are Legendre polynomials. Since  $\rho_H \ll 1$ , the second- and higher-order terms in  $\rho_H$  can be neglected. Then, Eq. (4) becomes

$$\begin{aligned} \left(\frac{\partial U}{\partial x}\right)_{x=0} &= D \exp\left(l - \frac{r}{a}\right) \left[ \frac{\rho_F}{a} \left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}} \right. \\ & \quad \sum_{n=0}^{\infty} (2n+1) I_{n+1/2}(\alpha) P_n(\cos \gamma) \cos \gamma \\ & \quad \left. - \frac{\rho_H}{a} \cos \gamma \right] - D \exp\left(\frac{l}{2} - \frac{r}{2a}\right) \\ & \quad \left[ \frac{\rho_F}{a} \left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}} \sum_{n=0}^{\infty} (2n+1) I_{n+1/2}\left(\frac{\alpha}{2}\right) \right. \\ & \quad \left. P_n(\cos \gamma) \cos \gamma - \frac{\rho_H}{a} \cos \gamma \right] \end{aligned} \quad (6)$$

in which  $P_n(\cos \gamma)$  is responsible  $j \rightarrow j \pm n$  rotational transitions. This expression indicates that the Ar-F interaction leads to  $j \rightarrow j \pm 1$  transitions only, but we can show in the numerical section below that the perturbation of the molecule due to the Ar-F interaction is negligible compared to the effect by the Ar-H encounter. The second term of Eq. (6) represents the effect of molecular attraction.

By introducing the recursion relation for  $P_n(\cos \gamma) \cos \gamma$ , we now write Eq. (6) in the form

$$\begin{aligned} \left(\frac{\partial U}{\partial x}\right)_{x=0} &= \frac{\rho_F}{a} \left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}} D \exp\left(l - \frac{r}{a}\right) \\ & \quad \left[ \sum_{n=0}^{\infty} (n+1) I_{n+3/2}(\alpha) P_n(\cos \gamma) \right. \\ & \quad \left. + \sum_{n=1}^{\infty} n I_{n-1/2}(\alpha) P_n(\cos \gamma) \right. \\ & \quad \left. - \frac{\rho_H}{\rho_F} \left(\frac{\partial \alpha}{\pi}\right)^{\frac{1}{2}} P_1(\cos \gamma) \right] \\ & - \frac{\rho_F}{a} \left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}} D \exp\left(\frac{l}{2} - \frac{r}{2a}\right) \\ & \quad \left[ \sum_{n=0}^{\infty} (n+1) I_{n+3/2}\left(\frac{\alpha}{2}\right) P_n(\cos \gamma) \right. \\ & \quad \left. + \sum_{n=1}^{\infty} n I_{n-1/2}\left(\frac{\alpha}{2}\right) P_n(\cos \gamma) \right. \\ & \quad \left. - \frac{\rho_H}{\rho_F} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} P_1(\cos \gamma) \right] \\ & \equiv \frac{\rho_F}{a} \left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}} \left[ D \exp\left(l - \frac{r}{a}\right) \right. \\ & \quad \sum_{n=0}^{\infty} f_n(\alpha) P_n(\cos \gamma) \\ & \quad \left. - 2^{\frac{1}{2}} D \exp\left(\frac{l}{2} - \frac{r}{2a}\right) \right. \\ & \quad \left. \sum_{n=0}^{\infty} f_n\left(\frac{\alpha}{2}\right) P_n(\cos \gamma) \right] \end{aligned} \quad (7)$$

where

$$\begin{aligned} f_0(x) &= I_{3/2}(x), \quad f_1(x) = 2I_{5/2}(x) + I_{1/2}(x) \\ & \quad - \frac{\rho_H}{\rho_F} \left(\frac{2x}{\pi}\right)^{\frac{1}{2}}, \\ f_n(x) &= (n+1) I_{n+3/2}(x) \\ & \quad + n I_{n-1/2}(x); \quad n \geq 2. \end{aligned}$$

In the region of strong interaction  $\exp\left(\frac{l}{2} - \frac{r}{2a}\right)$

is very small compared with  $\exp\left(l - \frac{r}{a}\right)$ , and furthermore  $f_n(\alpha/2)$  is smaller than  $f_n(\alpha)$  for given values of  $n$  and  $\alpha$ ; so the second term in Eq.(7) due to the inclusion of the molecular attraction term  $-2D \exp\left(\frac{l}{2} - \frac{r}{2a}\right)$  in  $U(r)$  may be neglected.

### 3. Transition Probabilities

**Simultaneous  $vj \rightarrow v'j'$  Transitions.** To derive the transition probabilities, we express the vibrational state by the function  $|v\rangle$  and the rotational states by  $|jm\rangle$ , which are spherical harmonics  $Y_{jm}(\gamma, \xi)$ ,  $\xi$  being the azimuthal angle defined in Fig. 1. The advantage of using these basis functions has been discussed in detail by Lawley and Ross<sup>4</sup> and recently by Sørensen<sup>5</sup>. The total wavefunction of the internal motion of the molecule can be expanded at time  $t$  in the unperturbed harmonic oscillator and rigid-rotor wavefunctions as

$$\phi(t) = \sum_{vm} |v\rangle |jm\rangle \exp\left[-\frac{i}{\hbar}(E_v + E_j)t\right] C_{vm, v'j'm'}(t) \quad (8)$$

where  $E_v = \hbar\omega\left(v + \frac{1}{2}\right)$  and  $E_j = (\hbar^2/2I)j(j+1)$ . The expansion coefficients  $C_{vm, v'j'm'}(t)$  determine the probability amplitudes for transition from the state  $(vm)$  to  $(v'j'm')$  at  $t$ . By introducing this expression into  $i\hbar(\partial/\partial t)\phi = H\phi$  and by use of the variation-of-constants procedure, Lawley and Ross obtained the following coupled equations<sup>4,5</sup>

$$i\hbar \frac{d}{dt} C(t) = \left[ A(t) - i\hbar U \frac{d}{dt} \theta(t) \right] C(t) \quad (9)$$

where the matrices  $A(t)$  and  $U$  are

$$A_{vm, v'j'm'}(t) = \langle v | \langle jm | \left( \frac{\partial U}{\partial x} \right)_{x=0} | j'm' \rangle | v' \rangle \exp\left[-\frac{it}{\hbar} \Delta E_{vj, v'j'}\right] \quad (10)$$

$$U_{vm, v'j'm'} = \delta_{vm, v'j'm'} \langle jm | \frac{\partial}{\partial \theta} | j'm' \rangle \quad (11)$$

with  $\Delta E_{vj, v'j'} = E_{v'} - E_v + E_{j'} - E_j$ . In Eq.(10), the rotational matrix element takes the form

$$\langle jm | P_n(\cos \gamma) | j'm' \rangle = (-)^m \begin{pmatrix} j & j' & n \\ -m & m' & 0 \end{pmatrix} \begin{pmatrix} j & j' & n \\ 0 & 0 & 0 \end{pmatrix} (2j+1)^{1/2} (2j'+1)^{1/2} \quad (12)$$

where the integration is over the angles  $\theta$  and  $\phi$ . In this expression the Wigner 3- $j$  symbols are related to Clebsch-Gordan coefficients as

$$\begin{pmatrix} abc \\ \alpha\beta\gamma \end{pmatrix} (2c+1)^{1/2} = (-)^{a-b-\gamma} \langle ab\alpha\beta | c-\gamma \rangle. \quad (13)$$

Sørensen gives the solution of Eq.(9) to the first order in  $A$ , i.e.,  $C^{(1)}(t)$ . With this solution, the transition probability ( $vj \rightarrow v'j'$ ) can be written as

$$P_{vj, v'j'} = \frac{1}{2j+1} \sum_{m, m'} |C_{vm, v'j'm'}^{(1)}(\infty)|^2 \quad (14)$$

For the present collision model we can obtain the matrix element in the form

$$A_{vm, v'j'm'}(t) = \left( \frac{2j'+1}{2j+1} \right)^{1/2} \underline{x}(\rho_F/a) (\pi/2\alpha)^{1/2} \sum_{n=0}^{\infty} \left[ D \exp\left(l - \frac{r}{a}\right) f_n(\alpha) - 2^{1/2} D \exp\left(\frac{l}{2} - \frac{r}{2a}\right) f_n(\alpha/2) \right] \langle nj'00 | j0 \rangle \langle j'nm'0 | jm \rangle \exp\left(-\frac{it}{\hbar} \Delta E_{vj, v'j'}\right) \quad (15)$$

where  $\underline{x} = \langle v | x | v' \rangle$ . It is sometimes convenient to use the 3- $j$  symbols instead of the vector addition coefficients. Using symmetry conditions and other useful relations<sup>5,6</sup> and neglecting intermultiplet transitions in Sørensen's formulation, we then obtain the transition probability for the present interaction system in the form

$$P_{vj, v'j'}(E, b) = (\pi/2\alpha) (\rho_F/a)^2 (x/\hbar)^2 (2j'+1) \sum_{n=0}^{\infty} \frac{1}{2n+1} \begin{pmatrix} j & j' & n \\ 0 & 0 & 0 \end{pmatrix}^2 \left[ f_n(\alpha) J_R(E, b) - (2D)^{1/2} f_n(\alpha/2) J_A(E, b) \right]^2 \quad (16)$$

where

$$J_R(E, b) = \int_{-\infty}^{\infty} D \exp\left(t - \frac{r}{a}\right) \exp(-it\Delta E/\hbar) dt \quad (17)$$

$$J_A(E, b) = \int_{-\infty}^{\infty} D^{\frac{1}{2}} \exp\left(\frac{l}{2} - \frac{r}{2a}\right) \exp(-it\Delta E/\hbar) dt \quad (18)$$

with  $\Delta E \equiv \Delta E_{v_j, v_{j'}}$ ; the subscripts "R" and "A" of  $J$  refer to the integrals due to repulsive and attractive interactions, respectively. In the above expressions,  $E$  is the initial relative energy and  $b$  the impact parameter.

**Trajectory.** We now proceed to the evaluation of the integrals given by Eqs. (17) and (18). In these integrals,  $r$  will have to be parameterized in time  $t$  through the solution of the equation of motion. A standard treatment of the dynamics of an encounter starts with the derivation of the trajectory  $r(t)$  from the equation which can be written as

$$t = (\mu/2)^{1/2} \int_{r^0}^r [E - E(b/r)^2 - U(r)]^{-1/2} dr \quad (19)$$

where  $\mu$  is the reduced mass of the collision system and  $r^0$  is the largest root of the radical in the denominator. The potential  $U(r)$  in this equation is given by Eq. (1). As  $r$  approaches zero, the interaction potential becomes strongly repulsive, i. e., the factor  $D \exp\left(t - \frac{r}{a}\right)$  in  $J_R$  or  $D \exp\left(\frac{l}{2} - \frac{r}{2a}\right)$  in  $J_A$  takes a very large value. To facilitate the calculation, we replace the integration along the real axis by an integration in the complex  $t$  plane. To carry out this integration, it is convenient to divide Eq. (19) into two terms:

$$t = i(\mu/2)^{1/2} \left[ \int_{r^*}^r (U(r) + E(b/r)^2 - E)^{-1/2} dr \right]$$

$$- \int_{r^*}^r (U(r) + E(b/r)^2 - E)^{-1/2} dr \quad (20)$$

The limits of integration suggest that the first integral is a time scale characteristic of the duration of collision. Therefore, we define

$$(\mu/2)^{1/2} \left[ \int_{r^*}^r U(r) + E(b/r)^2 - E)^{-1/2} dr \right]$$

as the collision time and denote it by  $\tau$ , which is a function of both  $E$  and  $b$ . In the region of strong interaction, the second integral can be approximated as  $\int_{r^*}^r (U(r))^{-1/2} dr$ , which can be integrated analytically; in the latter integrand we only need to include the repulsive term of  $U(r)$ . Then, the expression for  $t$  is

$$t = i\tau - ia(2\mu)^{\frac{1}{2}} \left[ D \exp\left(t - \frac{r}{a}\right) \right]^{-1/2} \quad (21-1)$$

or

$$D \exp\left(t - \frac{r}{a}\right) = -(2\mu a^2) (t - i\tau)^{-2} \quad (21-2)$$

It should be noted in Eq. (21-1) that the first term on the right-hand-side, i. e.,  $\tau$ , contains the effects of molecular attraction, while the second term does not. As will be shown below, the exponential part of  $P_{i, j, v_{j'}}(E, b)$  is solely determined by the first term.

In writing the time dependence of the integrand in  $J_R$  (and  $J_A$ ) we note that  $\Delta E$ , the inelasticity, is the internal energies that are taken away by the translational motion during the deexcitation process. For  $0j \rightarrow 1j'$  transitions, we have  $\Delta E = \hbar\omega + (\hbar^2/2I)(j'(j'+1) - j(j+1))$ , and for the  $1j \rightarrow 0j'$  deexcitation process  $\Delta E = -\hbar\omega + (\hbar^2/2I)(j'(j'+1) - j(j+1))$ . Both processes can be treated by a single expression of the inelasticity in obtaining the transition probabilities; we shall therefore write the exponential factor in  $J_R$  (and  $J_A$ ) by  $\exp(it|\Delta E|/\hbar)$ , where

$$|\Delta E| = |\hbar\omega + \frac{\hbar^2}{2I} (j'(j'+1) - j(j+1))|$$

For the excitation of both vibrational and rotational states, the energy supplied by the translational motion exceeds  $\hbar\omega$ . From the inelasticity expression given above it is obvious that lesser energies are involved for the excitation of the oscillator state accompanied by the deexcitation of rotational states so the probability associated with such processes can then be large.

In the complex  $t$  plane, the singularity occurs at  $t=i\tau$ , and  $r(t)$  determines the trajectory only in the neighborhood of  $i\tau$ . In many molecular collisions involving diatomic molecules,  $|\Delta E|\tau/\hbar \gg 1$ . For such cases, we can introduce Eq. (21-2) in  $J_R$  (or  $J_A$ ) to represent the entire integration path since the most important contribution to the integrand comes from an interval  $\tau$ . Then, the integral  $J_R$  now takes the specific form

$$J_R = -2\mu a^2 \int_{-\infty}^{\infty} \frac{\exp(it|\Delta E|/\hbar)}{(t-i\tau)^2} dt \quad (22)$$

Since there is a branch cut from  $i\tau$  along the imaginary axis to  $i\infty$ , the integral cannot be evaluated simply as the residue at the pole  $i\tau$ . However, it can be replaced by an integration along the contour, which extends from  $i\infty$ , encircles the singular point, and then follows the branch cut back out to  $i\infty$ .<sup>7</sup> The result of such a contour integration is

$$J_R = 4\pi\mu a^2 \frac{|\Delta E|}{\hbar} \exp\left(-\frac{|\Delta E|\tau}{\hbar}\right) \quad (23-1)$$

$$J_A = 2\pi(2\mu)^{\frac{1}{2}} a \exp\left(-\frac{|\Delta E|\tau}{\hbar}\right) \quad (23-2)$$

To complete the evaluation of the trajectory, it is now necessary to calculate the collision time  $\tau$ , which can be expressed as

$$\tau = \left(\frac{\mu}{2}\right)^{\frac{1}{2}} \int_V^E \frac{r'(V)dV}{(V-E)^{1/2}} \quad (24)$$

where  $V=U(r)+E(b/r)^2$  and  $r'(V)$  is the derivative of the inverse function  $r(V)$ . Since  $V^*$  is the potential energy evaluated at  $r^*$ , it is very large and can be taken as  $\infty$  in comparison with  $E$ . The inverse derivative  $r'(V)$  is difficult to derive because the potential is a sum of the exponential and inverse-power law terms. The inverse-power term contains the impact parameter, which should be included in calculating total transition probabilities. To avoid this operational difficulty, we first derive the collision time  $\tau_0$  for  $b=0$ , and then include the effect of nonzero- $b$  collisions by comparing  $\tau_0$  with that for the effective potential formulated as the sum of the Lennard-Jones(12-6) potential and the centrifugal energy term  $E(b/r)^2$ . This procedure of obtaining  $\tau$  is employed as the best of the alternatives. The inverse derivative obtained for  $b=0$  is

$$r'(V) = -\frac{1}{V} \sum_{i=0}^{\infty} \frac{\alpha_i}{V_i}; \quad \alpha_0 = a, \quad \alpha_{1/2} = -aD^{1/2}, \\ \alpha_1 = 0, \quad \alpha_{3/2} = \frac{aD^{3/2}}{2}, \quad \alpha_2 = 0, \dots \quad (25)$$

Upon substitution of this sum, Eq. (24) can be readily integrated to obtain

$$\tau_0 = \left(\frac{\pi\mu}{2}\right)^{1/2} \sum_{i=0}^{\infty} \frac{\Gamma(i+\frac{1}{2})}{\Gamma(i+1)} \frac{\alpha_i}{E^{i+1/2}} \quad (26)$$

For the effective potential  $V(r)=4D\{(\sigma/r)^{12} - (\sigma/r)^6\} + E(b/r)^2$ , the inverse derivative is

$$r'(V) = -\frac{1}{V^{13/12}} \sum_{i=0}^{\infty} \frac{\alpha_i}{V^i} \quad (27)$$

with

$$\alpha_0 = \frac{(4D)^{1/12}\sigma}{12}, \quad \alpha_{1/3} = -\frac{7}{144} (4D)^{7/12}\sigma,$$

$$\alpha_{5/6} = \frac{11}{144} \frac{b^2 E}{(4D)^{1/12}\sigma},$$

$$\alpha_1 = \frac{13}{3456} (4D)^{13/12}\sigma, \dots$$

If Eq. (27) is used in Eq. (24), it can be shown that

$$\tau_{LJ} = \left(\frac{\pi\mu}{2}\right)^{\frac{1}{2}} \sum_{i=0}^{\infty} \frac{\Gamma\left(i + \frac{7}{12}\right)}{\Gamma\left(i + \frac{13}{12}\right)} \frac{\alpha_i}{E^{7/12+i}} \quad (28)$$

in which the term due to the centrifugal potential  $E(b/r)^2$  is

$$\tau_b = \frac{5}{144} \frac{\Gamma\left(\frac{5}{12}\right)}{\Gamma\left(\frac{11}{12}\right)} \left(\frac{\pi\mu}{2}\right)^{\frac{1}{2}} \frac{b^2}{\sigma(4D)^{1/12} E^{5/12}} \quad (29)$$

Then, the collision time in the present model can be expressed as  $\tau = \tau_0 + \tau_b$ .

The complete expression for the transition probabilities is

$$P_{vj, v'j'}(E, b) = \left(\frac{\pi}{2\alpha}\right) \left(\frac{\rho_F}{a}\right)^2 \left(\frac{x}{\hbar}\right)^2 (2j'+1) \left(\frac{4\pi\mu a^2 |\Delta E|}{\hbar}\right)^2 \exp\left[-\frac{(2\mu)^{1/2} \pi |\Delta E|}{\hbar}\right] \left(\frac{\alpha_0}{E^{1/2}} + \frac{2\alpha_{1/2}}{\pi E} + \frac{4\alpha_{3/2}}{3\pi E^2} + \dots\right) - \frac{5}{144} (2\pi\mu)^{1/2} \frac{\Gamma\left(\frac{5}{12}\right)}{\Gamma\left(\frac{11}{12}\right)} \frac{|\Delta E| b^2}{\sigma(4D)^{1/12} \hbar E^{5/12}} \sum_{n=0}^{\infty} \binom{j \ j' \ n}{0 \ 0 \ 0}^2 \frac{1}{(2n+1)} \left[ f_n(\alpha) - \frac{\hbar}{a |\Delta E|} \left(\frac{D}{\mu}\right)^{\frac{1}{2}} f_n\left(\frac{\alpha}{2}\right) \right]^2 \quad (30)$$

With this expression the total transition probability is defined as

$$P_{vj, v'j'}(E) = \frac{1}{\pi r^{*2}} \int_0^{\infty} 2\pi P_{vj, v'j'}(E, b) b db \quad (31)$$

where  $r^*$  is a characteristic distance at which the transitions are most likely to take place. (We shall determine this distance in the following section.) In Eqs. (30) and (31) the  $b$ -integral is simply

$$\frac{1}{\pi r^{*2}} \int_0^{\infty} 2\pi \exp\left(-\frac{2|\Delta E| \tau_b}{\hbar}\right) b db = \frac{144}{5} \frac{\Gamma\left(\frac{11}{12}\right)}{\Gamma\left(\frac{5}{12}\right)} \frac{\sigma(4D)^{1/12} \hbar E^{5/12}}{(2\pi\mu)^{1/2} r^{*2} |\Delta E|} \quad (32)$$

**Thermal Average of  $P_{vj, v'j'}(E)$ .** We shall average  $P_{vj, v'j'}(E)$  over a Boltzmann distribution of the initial collision energies and sum over the rotational states to derive the thermal average transition probability

$$P_{01}(T) = \frac{T}{\Theta_r} \sum_{j,j'} (2j+1) \exp\left[-\frac{\Theta_r}{T} j(j+1)\right] \int_0^{\infty} \frac{E}{(kT)^2} P_{vj, v'j'}(E) \exp\left(-\frac{E}{kT}\right) dE, \quad (33)$$

where  $\Theta_r = \hbar^2/2Ik$ ,  $I$  being the moment inertia of the molecule. By substituting Eq. (30) into this expression, we find that the essential part of the  $E$ -integral is

$$\mathcal{J}_E = \int_0^{\infty} \frac{E^{17/12}}{(kT)^2} \exp\left[-\frac{(2\mu)^{1/2} \pi |\Delta E|}{\hbar}\right] \left(\frac{\alpha_0}{E^{1/2}} + \frac{2\alpha_{1/2}}{\pi E} + \frac{4\alpha_{3/2}}{3\pi E^2}\right) \exp\left(-\frac{E}{kT}\right) dE, \quad (34)$$

showing a product of two exponential factors with opposite dependence on  $E$ . The first factor, which came from the transition probability, increases very rapidly as  $E$  is increased, while the second factor multiplied by  $E$  represents the Boltzmann distribution, possesses a maximum at a moderate value of  $E$ , and decreases sharply as  $E$  increases in the range of physical interest. The integrand, therefore, possesses a sharp maximum value at  $E = E^*$ , which is higher than the energy at which the Boltzmann distribution takes a maximum value. This situation indicates that the high-energy "tail" section of the Boltzmann distribution is mainly responsible for the energy transfer. By denoting the

exponent of Eq. (34) by  $g(E)$  and replacing the slowly varying preexponential part by  $E^{*17/12}$ , we can evaluate the integral approximately as

$$J_E = \left[ \frac{2\pi}{|g'(E^*)|} \right]^{1/2} E^{*17/12} \exp(g(E^*)). \quad (35)$$

From  $g'(E^*)=0$ , we find

$$E^* = \chi - \frac{8}{3\pi} (D\chi)^{1/2} - \frac{16D}{3\pi^2} \quad (36)$$

where

$$\chi = \left[ \left( \frac{\mu}{2} \right)^{1/2} \frac{\pi |\Delta E| a k T}{\hbar} \right]^{2/3}$$

i. e.,  $\chi$  depends on the inelasticity. When  $g(E^*)$  and  $g'(E^*)$  are evaluated at  $E=E^*$  given by Eq. (36) and are introduced in Eq. (35) we obtain

$$J_E = \left( \frac{4\pi}{3} \right)^{1/2} \left( \frac{\chi}{kT} \right)^{3/2} \chi^{5/2} \exp \left[ -\frac{3\chi}{kT} + \frac{4(D\chi)^{1/2}}{\pi kT} + \frac{16D}{3\pi^2 kT} \right]. \quad (37)$$

To simplify the overall result, we use the following expression<sup>8</sup> which relates the exponential range parameter  $a$  to the Lennard-Jones constant  $\sigma$ :

$$\sigma = a\pi^{1/2} \frac{\Gamma(1/12)}{\Gamma(7/12)} \left( \frac{\chi}{4D} \right)^{1/2}. \quad (38)$$

The coefficient of  $E^{5/12}$  in Eq. (32) can be written as

$$\frac{72}{5} \frac{\Gamma(11/12)}{\Gamma(5/12)} \frac{\pi^{1/2} (4D)^{1/12} \sigma a k T}{r^{*2} \chi^{3/2}}.$$

When the Lennard-Jones constant  $\sigma$  in this coefficient is replaced by Eq. (38), we find

$$\frac{72}{5} \frac{\Gamma(11/12)}{\Gamma(5/12)} \frac{\Gamma(1/12)}{\Gamma(7/12)} \frac{\pi a^2 k T}{r^{*2} \chi^{17/12}}.$$

The factor  $\chi^{5/12}$  appearing in Eq. (37) came

from  $E^{5/12}$  in Eq. (32), so the inclusion of all possible nonzero- $b$  collisions leads to the appearance of the following factor in the preexponential part of  $P_{10}(T)$ :

$$c\pi (a/r^*)^2 (kT/\chi)$$

where

$$c = \frac{72}{5} \frac{\Gamma(11/12)}{\Gamma(5/12)} \frac{\Gamma(1/12)}{\Gamma(7/12)} = 53.7.$$

We also note that the product of Eq. (32) evaluated at  $E=E^*$  and the preexponential part of Eq. (37) is

$$(4\pi/3)^{1/2} (\chi/kT)^{1/2} c\pi (a/r^*)^2.$$

Therefore, the final expression of the thermal average transition probability is

$$P_{01}(T) = \frac{T}{2M\hbar\omega\theta_r} \left( \frac{\pi}{2\alpha} \right) (4\pi\rho_F\mu a)^2 \left( \frac{4\pi}{3} \right)^{1/2} c\pi \left( \frac{a}{r^*} \right)^2 \exp \left( \frac{16D}{3\pi^2 kT} \right) \sum_{j,j'} (2j+1)(2j'+1) \exp \left[ -\frac{\theta_r}{T} j(j+1) \right] \left( \frac{|\Delta E|}{\hbar} \right)^2 \left( \frac{\chi}{kT} \right)^{1/2} \exp \left[ -\frac{3\chi}{kT} + \frac{4(D\chi)^{1/2}}{\pi kT} - \frac{|\Delta E|}{2kT} \right] \sum_{n=0}^{\infty} \binom{j \ j' \ n}{0 \ 0 \ 0}^2 \frac{1}{(2n+1)} [f_n(\alpha)]^2 [1-b_n(\alpha)]^2 \equiv \sum_{j,j'} P_{0j1j'}(T), \quad (39)$$

with

$$b_n(\alpha) = \frac{\hbar}{a|\Delta E|} \left( \frac{D}{\mu} \right)^{1/2} \frac{f_n(\alpha/2)}{f_n(\alpha)},$$

where the vibrational matrix element is expressed as  $\underline{x} = \hbar/(2M\hbar\omega)^{1/2}$ ,  $M$  being the reduced mass of the oscillator. Since  $E$  is the relative energy before excitation of the molecule, the final energy is  $E - |\Delta E|$ , so that we can write the symmetrized energy as  $E - \frac{1}{2}|\Delta E|$ . The term  $-|\Delta E|/2kT$  in the exponent of Eq. (39) is due to this symmetrization. Equation (39) describes the transition process in which the oscillator is excited from  $v=0$  to 1. To obtain



the thermal average transition probability appropriate to deexcitation of the oscillator, i. e.,  $P_{10}(T)$ , rather than to an excitation, we have merely to replace  $-|\Delta E|/2kT$  by  $+|\Delta E|/2kT$ . In the following section we shall calculate this probability.

In Eq. (39), the exponential factors  $\exp[4(D\gamma)^{1/2}/\pi kT]$  and  $\exp(16D/3\pi^2 kT)$  are due to the inclusion of the attractive potential term  $-2D \exp\left(\frac{l}{2} - \frac{r}{2a}\right)$  in calculating the collision time. While the second factor is normally not significantly different from unity, the first factor can be very large and in some cases can even increase the transition probability by more than an order of magnitude. The term  $b_n(\alpha)$  in the  $n$  sum is also due to the attractive energy, but it is usually very small compared to unity. If the purely repulsive potential  $U(r) = D \exp\left(l - \frac{r}{a}\right)$  were assumed, the resulting expression of  $P_{10}(T)$  would be identical to Eq. (39) except that the  $D$ -dependent terms in the exponent and  $b_n(\alpha)$  in the preexponential part are now set equal to zero.

#### 4. Numerical Results and Discussion

We now calculate  $P_{10}(T)$  at 300 °K by taking the following molecular parameters:<sup>9-11</sup>  $d_0 = 0.917$  Å,  $\omega = 7.475 \times 10^{14}$  sec<sup>-1</sup>,  $D/k = 223$  °K which is obtained from  $D_{HF}/k = 400$  °K and  $D_{Ar}/k = 124$  °K by use of the combining law, and  $\sigma = 2.906$  Å from  $\sigma_{HF} = 2.394$  Å and  $\sigma_{Ar} = 3.418$  Å. The distance  $r^*$  is calculated from the expression<sup>12</sup>

$$r^* = \left[ \frac{14\sigma^6}{\omega} \left( \frac{2D}{\mu} \right)^{1/2} \right]^{1/3}$$

as 1.83 Å. The exponential range parameter is obtained from Eq. (38) as 0.187 Å. When these values are used, the factor appearing in Eq.

(39) as the coefficient of the  $j, j'$  and  $n$  sums is  $1.70 \times 10^{-24}$  sec<sup>2</sup>.

The energy term  $\chi$  is proportional to the inelasticity as  $\chi \propto |\Delta E|^{2/3} \equiv |\Delta E_{vj, v'j'}|^{2/3}$ , so the  $j, j'$  sums in Eq. (39) appear in complicated forms. Although it is somewhat lengthy, a term-by-term calculation of these sums is straightforward. The calculation of 3- $j$  symbols is in general tedious, but those appearing in Eq. (39) are in particularly simple forms. For  $j+j'+n$  is odd, the coefficient is zero, and for  $j+j'+n$  is even, it is<sup>13</sup>

$$\left( \begin{matrix} j & j' & n \\ 0 & 0 & 0 \end{matrix} \right)^2 = \{ \Delta(jj'n)g! / [(g-j)!(g-j')!(g-n)!] \}^2$$

where  $g = (j+j'+n)/2$  and

$$\Delta(jj'n) = \left[ \frac{(j+j'-n)!(j+n-j')!(j'+n-j)!}{(j+j'+n+1)!} \right]^{1/2}$$

The modified Bessel functions of low orders can be readily calculated; for higher orders it is convenient to use the relation<sup>14</sup>

$$I_n + \frac{1}{2}(\alpha) = \frac{1}{(2\pi\alpha)^{1/2}} \left[ \exp(\alpha) \sum_{r=0}^{\infty} \frac{(-)^r (n+r)!}{r! (n-r)! (2\alpha)^r} + (-)^{n+1} \exp(-\alpha) \sum_{r=0}^{\infty} \frac{(n+r)!}{r! (n-r)! (2\alpha)^r} \right]$$

The squared quantity  $(f_n(\alpha))^2 [1 - b_n(\alpha)]^2$  appearing in the preexponential part of Eq. (39) takes the values of 237, 1510, 2100, and 1120 for  $n=0, 1, 2$ , and 3, respectively. However, as  $n$  increases the values decrease rapidly; e. g., for  $n=4, 5$ , and 6, we find 574, 170, and 27.3, respectively. Furthermore, these quantities are multiplied by  $(2n+1)^{-1} \left( \begin{matrix} j & j' & n \\ 0 & 0 & 0 \end{matrix} \right)^2$ , which becomes small as  $n$  increases. From Eqs. (5) and (12), it can be shown that for  $0j \rightarrow 1j$ , the first  $j+1$  terms in the  $n$ -sum with even values of  $n$  including zero contribute to the overall value of  $P_{10}(T)$  but the main contribution comes from the  $n=0$  term. For  $0j \rightarrow 1j$

Table 1. Calculated values of  $P_{j, j'}(T)$  at 300°K

	$j'=0$	1	2	3	4	5	6	7	8	9
$j=0$	.434 <sup>a</sup>	.948	.832	.352	.153	.044	.007	.001	.000	.000
1	.740	1.97	1.90	1.42	.520	.239	.072	.010	.002	.000
2	.393	1.16	1.78	1.86	1.42	.558	.254	.082	.017	.000
3	.077	.414	.881	1.33	1.36	1.05	.410	.207	.072	.016
4	.008	.056	.246	.509	.776	.779	.602	.264	.134	.052
5	.000	.007	.029	.117	.226	.334	.280	.279	.121	.070
6	.000	.000	.003	.010	.039	.078	.117	.126	.102	.047
7	.000	.000	.000	.000	.003	.010	.022	.032	.035	.030
8	.000	.000	.000	.000	.000	.000	.002	.005	.007	.007

<sup>a</sup> Values are in  $10^{-7}$ .

$\pm n$  ( $n \geq 1$ ) transitions, the first  $k-n+1$  terms of the sum are nonvanishing, where  $k$  is the larger of  $j, j'$ ; the first several terms are associated with  $n, n+2, n+4, \dots$

Symbolically we can write Eq. (39) as  $P_{10}(T) = \sum_{j, j'} P_{1j, 0j'}(T)$  for the deexcitation process. (Note that the sum of all possible  $j \rightarrow j \pm n$  rotational contributions can be expressed as  $\sum_{j, n} P_{1j, 0j \pm n}(T)$ .) Listed in Table 1 are the values of these individual  $j, j'$  terms of  $P_{10}(T)$ , i.e.,  $P_{1j, 0j'}(T)$ . Therefore, the sum of the values listed in Table 1 is the probability of the vibrational deexcitation ( $1 \rightarrow 0$ ) including all possible rotational transitions ( $j \rightarrow j, j \rightarrow j+n$ , and  $j \rightarrow j-n$ ). The values shown on the upper-right side of the diagonal entries represent  $j \rightarrow j+n$  so the inelasticity  $|\Delta E|$  is less than the vibrational quantum  $\hbar\omega$ . In these simultaneous vibrational and rotational transition processes, a portion of the vibrational energy is transferred to the rotational motion causing  $j \rightarrow j+n$  excitations, and the remaining energy is removed by the translational motion. The lower-left values are for  $j \rightarrow j-n$ , which are associated with  $|\Delta E| > \hbar\omega$ ; in this case both vibrational and rotational energies are transferred to the translational motion. The diagonal entries represent purely vibrational transitions, i.e.,  $j \rightarrow j$  or  $\Delta j=0$ .

For  $\Delta j=0$ , the leading term in the exponent

$-3\chi/kT$  is  $-51.6$ , while  $4(D\chi)^{1/2}/\pi kT$  and  $16D/3\pi^2 kT$  are 4.55 and 0.401, respectively. The factor  $[1-b_n(\alpha)]^2$  in the preexponential part is 0.961 so the overall effect of molecular attraction is to increase  $P_{10}(T)$  obtained for purely repulsive interaction  $U(r) = D \exp\left(l - \frac{r}{a}\right)$  by a factor of  $0.961 \exp(5.06) = 151$ .

We should point out the importance of non-zero- $b$  collisions in the deexcitation process. The inclusion of these collisions causes the factor  $c\pi(a/r^*)^2(kT/\chi)$  to appear in the preexponential part of  $P_{10}(T)$ . For example, the numerical values of this factor is 0.102 for  $\Delta j=0$ .

The function  $f_1(\alpha)$ , which includes the effect of both Ar-H and Ar-F interactions, is  $2I_{5/2}(\alpha) + I_{1/2}(\alpha) - (\rho_H/\rho_F)(2\alpha/\pi)^{1/2}$  and takes the numerical value of 38.9. Of these three terms, the last one comes from the Ar-F interaction and its value is only 0.090, so this interaction makes a negligible contribution to the overall transition process.

Several important results on the contribution of rotational transitions to the  $1 \rightarrow 0$  vibrational deexcitation process in HF-Ar are as follows. (i) As shown in Table 1, the contribution of  $\Delta j=0$  rotational processes to the value of  $P_{10}(T)$  is important but is not the largest. The largest contribution (38%) comes from  $j \rightarrow j \pm 1$  proce-

ses, the  $j \rightarrow j+1$  contribution being more than twice that of  $j \rightarrow j-1$ , while only 23 % is due to  $j \rightarrow j$  transitions. The  $\Delta j = \pm 2$  processes are also very important; the sum of the contributions coming from  $j \rightarrow j+2$  and  $j \rightarrow j-2$  is about 24 % of the overall value of  $P_{10}(T)$ . The 8 % contribution comes from  $j \rightarrow j \pm 3$ . Less than 7 % of  $P_{10}(T)$  is due to the remaining higher-order rotational transitions. In Fig. 2, we show the values of these individual contributions, i. e.,  $\sum_j P_{1j, 0j \pm n}$  as a function of  $n$ . Therefore,

in the present model, the inclusion of rotational transitions with  $\Delta j = \pm n$ ,  $n \geq 1$ , increases the transition probability  $P_{10}(T)$  obtained for  $\Delta j = 0$  by a factor of about 4.3. (ii) Because of the rotational distribution function appearing in Eq. (33) takes large values between  $j=1$  and 3, the  $j=2$  giving the largest value, individual terms in the  $j, j'$  sums with the initial rotational quantum numbers  $j=1, 2$ , and 3 are larger than those with others; see Fig. 3 for the relative populations of the rotational levels at 300 °K.

(iii) For  $1j \rightarrow 0j - n$  deexcitation process, the transition probabilities rapidly become small as  $n$  gets larger than 3, because more internal energies have to be carried away by the translational motion, which is an inefficient process. (iv) Table 1 shows that it is necessary to include many terms of both  $j, j'$  and  $n$  sums to obtain thermal average transition probability. At least all terms up to  $j=8$  with  $\Delta j = \pm 5$  have to be included in the calculation of  $P_{10}(T)$ . The contribution of  $1j \rightarrow 0j \pm 6$  is about 0.2 % of  $P_{10}(T)$ . In addition, it is necessary to include  $n$  from zero to at least six for the  $n$  sum, but as pointed out above some of these terms vanish.

The  $j, j'$  sums of the values listed in Table 1 or the  $j, n$  sums of those shown in Fig. 2 give the overall transition probability  $P_{10}(T) = 2.87 \times 10^{-6}$ . Only low temperature experimental data available at present give  $P_{10}(T) = 8.3 \times 10^{-6}$  at

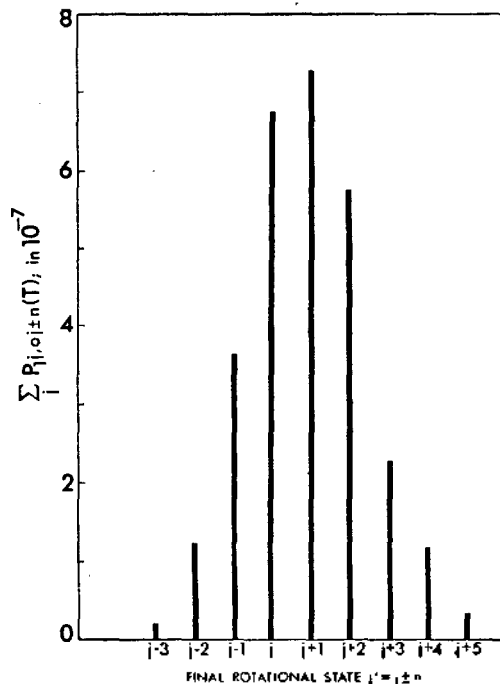


Fig. 2. The heavy-line ordinates give the values of  $\sum_j P_{1j, 0j \pm n}$  for various final states  $j \pm n$  (i. e., for different values of  $n$ ). The sum of these values over  $n$  is  $P_{10}(T)$ .

294 °K, which is reported by Hancock and Green<sup>1c</sup>. Since this is the *upper-limit* value<sup>1c</sup>, it is not possible to make a meaningful comparison with the present calculation, but the agreement is reasonable. Another experimental study reported by Bott and Cohen<sup>1c</sup> covers the temperature range of 1300 to 4000 °K, but a simple extrapolation of their data to room temperature cannot be made because of the increased importance of molecular attraction at lower temperatures.

A final comment is in order concerning the use of conventional VT energy transfer theories<sup>2</sup> to calculate  $P_{10}(T)$ . To study the problem of purely VT energy transfer processes with such theories, we average the potential derivative given by Eq. (4) over  $\gamma$ :

$$\left(\frac{\partial U}{\partial x}\right)_{x=0} = \frac{1}{d_0} \left\{ \left[ \cos h\left(\frac{\rho_F d_0}{a}\right) - \left(\frac{a}{\rho_F d_0}\right) \right] \right\}$$

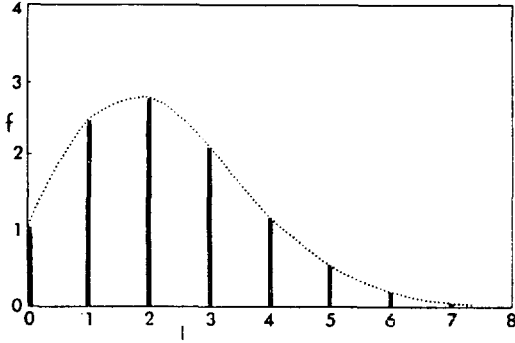


Fig. 3. Thermal distribution of the rotational levels for 300 °K. The curve represents the distribution

$f = (2j+1) \exp[-\theta_r j(j+1)/T]$  as a function of  $j$ . The heavy-line ordinates give the relative population of the corresponding rotational levels.

$$\begin{aligned}
 & \left[ \sin h\left(\frac{\rho_F d_0}{a}\right) \right] + \left[ \cos h\left(\frac{\rho_H d_0}{a}\right) \right. \\
 & \left. - \left(\frac{a}{\rho_H d_0}\right) \sin h\left(\frac{\rho_H d_0}{a}\right) \right] \Big\} D \exp\left(t - \frac{r}{a}\right) \\
 & - \frac{1}{d_0} \left\{ \left[ \cos h\left(\frac{\rho_F d_0}{2a}\right) - \left(\frac{2a}{\rho_F d_0}\right) \right. \right. \\
 & \left. \left. \sin h\left(\frac{\rho_F d_0}{2a}\right) \right] + \left[ \cos h\left(\frac{\rho_H d_0}{2a}\right) \right. \right. \\
 & \left. \left. - \left(\frac{2a}{\rho_H d_0}\right) \sin h\left(\frac{\rho_H d_0}{2a}\right) \right] \right\} \\
 & D \exp\left(\frac{t}{2} - \frac{r}{2a}\right). \quad (40)
 \end{aligned}$$

Since  $-\left(\frac{\partial U}{\partial x}\right)_{x=0}$  is the perturbing force, we can write the classical expression<sup>3a</sup> for the 0→1 transition probability per collision as the amount of vibrational energy transfer divided by  $\hbar\omega$ :

$$P_{01}(E, b) = \frac{1}{\hbar\omega} \left| \frac{1}{2M} \int_{-\infty}^{\infty} \left(\frac{\partial U}{\partial x}\right)_{x=0} \exp(i\omega t) dt \right|^2. \quad (41)$$

The average of this expression over the impact parameter is

$$P_{01}(E) = \frac{1}{M\hbar\omega r^{*2}} \int_0^{\infty} b db \left| \int_{-\infty}^{\infty} \left(\frac{\partial U}{\partial x}\right)_{x=0} \exp(i\omega t) dt \right|^2. \quad (42)$$

Using the procedure described above to obtain Eqs. (30)~(39), we now find the thermal average probability for the 1→0 deexcitation process as

$$\begin{aligned}
 P_{10}(T) &= \frac{1}{M\hbar\omega r^{*2} (kT)^2} \int_0^{\infty} E \exp(-E/kT) dE \\
 & \int_0^{\infty} b db \left| \int_{-\infty}^{\infty} \left(\frac{\partial U}{\partial x}\right)_{x=0} \exp(i\omega t) dt \right|^2 \\
 &= \frac{8\omega}{\hbar M} \left(\frac{\pi\mu a^2}{d_0}\right)^2 Q^2 \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \left(\frac{\chi}{kT}\right)^{\frac{1}{2}} \\
 & c\pi \left(\frac{a}{r^*}\right)^2 \exp\left[-\frac{3\chi}{kT} + \frac{4(D\chi)^{1/2}}{\pi kT} \right. \\
 & \left. + \frac{16D}{3\pi^2 kT} + \frac{\hbar\omega}{2kT}\right] \quad (43)
 \end{aligned}$$

where

$$\begin{aligned}
 Q &= \left[ \cos h\left(\frac{\rho_F d_0}{a}\right) - \left(\frac{a}{\rho_F d_0}\right) \sin h\left(\frac{\rho_F d_0}{a}\right) \right] \\
 & + \left[ \cos h\left(\frac{\rho_H d_0}{a}\right) - \left(\frac{a}{\rho_H d_0}\right) \sin h\left(\frac{\rho_H d_0}{a}\right) \right]
 \end{aligned}$$

and a small term in the preexponential part representing the effect of molecular attraction is neglected. Here  $|dE|$  is simply  $\hbar\omega$ . We note that when the WKB wavefunctions are used in the distorted wave approximation<sup>15</sup> for the perturbation energy given by  $\left(\frac{\partial U}{\partial x}\right)_{x=0} x$ , we obtain the same result. Equation(43) gives the numerical value  $2.74 \times 10^{-9}$  at 300 °K, which is smaller than the value obtained from Eq. (39) by three orders of magnitude. It may be noted that the SSH theory<sup>16</sup> would lead to even smaller values, because it usually introduces the effect of molecular attraction by  $+D/kT$  in the exponent; i.e., in the SSH theory, the exponential part of  $P_{10}(T)$  is  $\exp(-3\chi/kT + D/kT + \hbar\omega/2kT)$ . At 300 °K,  $\exp(D/kT) = 2.10$ , while  $\exp(4(D\chi)^{1/2}/\pi kT + 16D/3\pi^2 kT) = 142$ , so the simple modification of  $P_{10}(T)$  by  $\exp(D/kT)$  for the contribution of molecular attraction in the SSH theory leads to the transition probability which is smaller than that obtained from Eq. (43) by a factor of about 67. Therefore, the SSH value is nearly five orders of magnitude

smaller than the probability obtained from Eq. (39).

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