Temperature Dependence of the Rate Constants of the VV Energy Exchange for $N_2(v=1)+O_2(v=0)\rightarrow N_2(v=0)+O_2(v=1)$

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The vibration-vibration energy exchange of $N_2(v=1)+O_2(v=0)\rightarrow N_2(v=0)+O_2(v=1)$ has been investigated, in particular, at low temperatures. The energy exchange rate constants are calculated by use of the solution of the time-dependent Schrödinger equation with the interaction potential of the colliding molecule as a perturbation term. The predicted rate constants are significantly agree with a experimental values in the range of 295∼90°K. The consideration of the VV-VT coupling decreases the predicted pure VV energy exchange value by a factor of ∼2. When the collision frequency correction is introduced, the VV-VT rate constant is consistent with the observed value in the liquid phase. The consideration of the population of the rotational energy level increases the VV-VT value significantly.

Introduction

Information on the temperature dependence of vibrational energy exchange in diatomic molecules at high temperatures is well documented but such information is sparse near and below room temperature, including the liquid state. But, recently, there has been a growing number of experiments performed in which the vibrational relaxation of small, nonpolar molecules in the liquid state is measured. One such system is $N_2(v=1)$-O_2 system, whose liquid state has been the subject of extensive discussion in recent years.[1,2] Then, it has been shown that the dependence of rate constants on temperature is quite different at low temperatures compared with that at high temperatures. Thus, extra polations from high to lower temperatures are likely to give misleading results.[3,4] At present, theoretical calculations cannot be used to predict rate constants at low temperatures.[5] This is partly due to the lack of accurate information on intermolecular potentials. Deviations from the Landau-Teller relation[6] $\log(P)\sim T^{-1/3}$ become increasingly pronounced at low temperatures, with the probabilities being greater than predicted. This effect may be due to attractive forces which can affect both the probability of deactivation per collison and the number of trajectories leading to collisions. Although the gas-phase theory based on a binary-collision model is not expected to describe vibrational relaxation in the liquid state adequately, it should be instructive to extend such a model at least down to near the boiling point, at which the experimental data are now becoming available.[1] Among the existing theoretical approaches to gas-phase collisions is the semiclassical method, which we have outlined three years ago.[7] We shall use it here to determine the temperature dependence of the vibrational relaxation process over 90-300°K. On the other hand, in the vibrational relaxation process two processes, i.e., VT and VV are dominant, but VT deactivation of $N_2(v=1)$ by O_2 is too small to contribute to the vibrational relaxation considerably under the temperature range mentioned above. Therefore we shall neglect the VT deactivation and consider that the vibrational relaxation is proceeded only by the VV deactivation.

Interaction Potential and Energy Transfer Rate Constant

For the collision of two diatomic molecules N_2 and O_2, the potential energy of the interaction will be assumed as a Morse type composed of four atom-atom interactions. That is,

$$U(r_1,r_2,r_3,r_4)=\frac{1}{4}\sum_{i=1}^{4}U(r_i) \tag{1}$$

where $U(r_i)=D\{\exp[(r_{ie}-r_i)/a]-\frac{1}{2}\exp[(r_{ie}-r_i)/2a]\}$; D measures the depth of the potential well and a is the potential range parameter. Here r_{ie}'s are the equilibrium values of r_i's which are the distances between atoms. For the distance r between the centers of mass significantly greater than the equilibrium bond distance d(*i. e.*, d_1 and d_2 for molecule 1 or 2), the atom-atom distances can be approximated as $r_{1,2}=r-\frac{1}{2}(d_1+q_1)\cos\theta_1\pm\frac{1}{2}(d_2+q_2)\cos\theta_2$ and $r_{3,4}=r+\frac{1}{2}(d_1+q_1)\cos\theta_1\pm\frac{1}{2}(d_2+q_2)\cos\theta_2$ where θ_i is the angle between the molecular axis and r. Because $r_i=r_i(r,q_1,q_2,\theta_1,\theta_2)$, the overall potential can be represented by $U(r_1,r_2,r_3,r_4)=U(r,q_1,q_2,\theta_1,\theta_2)$. Then the interaction potential can be expressed in the form:

$$\begin{aligned}U(r,q_1,q_2,\theta_1,\theta_2)&=U(r,0,0,\theta_1,\theta_2)+q_1(\partial U/\partial q_1)_0\\&+q_2(\partial U/\partial q_2)_0+\frac{1}{2}q_1^2(\partial^2U/\partial q_1^2)_0+\frac{1}{2}q_2^2(\partial^2U/\partial q_2^2)_0\\&+q_1q_2(\partial^2U/\partial q_1\partial q_2)_0+\cdots\end{aligned} \tag{2}$$

where all derivatives are evaluated at $q_1=q_2=0$. As it will be shown later, we shall replace the q_1, q_2 coordinates by the boson operators $(a_i^{\dagger},a_i)$. If this is done, the terms involving q_1^2, q_2^2 will be converted into the forms of $a_i^{\dagger 2}$ and a_i^2, which are "two-quantum" VT operators since they produce or eliminate two vibrational quanta at a time. Moreover, here, we can simplify $U(r,q_1,q_2,\theta_1,\theta_2)$ by neglecting this "two-quantum" VT operators. This does not imply that multiquantum VT excitation is eliminated but rather implies that a two-quantum transition, for instance, occurs through two one-quantum jumps, rather than by a direct two quantum jumps. As demonstrated in previous paper,[8] the latter process is in fact more than two orders of magnitude less probable than the former for almost any diatomic molecule except in very energetic collisions, so that neglecting the "two-quantum" operators in $U(r,q_1,q_2,\theta_1,\theta_2)$ is not a very restrictive approximation.

We can, thus, now write if it truncated to second order,

$$U(r,q_1,q_2,\theta_1,\theta_2)=U(r,0,0,\theta_1,\theta_2)+q_1(\partial U/\partial q_1)_0 + q_2(\partial U/\partial q_2)_0+q_1q_2(\partial^2U/\partial q_1\partial q_2)_0 \quad (3)$$

When all derivatives are evaluated, the result of $U(r,q_1,q_2,\theta_1,\theta_2)$ is summarized as follows[7]:

$$\begin{aligned}U(r,q_1,q_2,\theta_1,\theta_2)=\frac{1}{4}\sum_{i=1}^{4}[&U_0^i(r,\theta_1,\theta_2)+U_1^i(r,q_1,\theta_1,\theta_2)\\ &+U_2^i(r,q_2,\theta_1,\theta_2)+U_{12}^i(r,q_1,q_2,\theta_1,\theta_2)]\\ \equiv{}&U_0(r,\theta_1,\theta_2)+U_1(r,q_1,\theta_1,\theta_2)\\ &+U_2(r,q_2,\theta_1,\theta_2)+U_{12}(r,q_1,q_2,\theta_1,\theta_2)\end{aligned} \quad (4)$$

For the present VV energy exchange process with the energy mismatch transferred to translation, the appropriate form of the total interaction energy obtained from the above approximation is

$$U(r,q_1,q_2,\theta_1,\theta_2)=U_0(r,\theta_1,\theta_2)+U_{12}(r,q_1,q_2,\theta_1,\theta_2) \quad (5)$$

On the other hand, for the present VV energy transfer, the removal of ΔE by the rotational degree of freedom is not important. The rotation, however, will certainly affect the collision dynamics, and hence, energy exchange probabilities; we shall replace this effect by the rotation average as shown below.

$$\overline{U}_0(r)=\frac{1}{4}\int_0^{\pi}\int_0^{\pi}U_0(r,\theta_1,\theta_2)\sin\theta_1\sin\theta_2 d\theta_1 d\theta_2 \quad (6)$$

and

$$\overline{U}_{12}(r,q_1,q_2)=\frac{1}{4}\int_0^{\pi}\int_0^{\pi}U_{12}(r,q_1,q_2,\theta_1,\theta_2)\sin\theta_1\sin\theta_2 d\theta_1 d\theta_2 \quad (7)$$

Then,

$$\overline{U}_0(r)=D^*[\exp(\frac{r_e^*-r}{a})-2\exp(\frac{r_e^*-r}{2a})] \quad (8)$$

$$\overline{U}_{12}(r,q_1,q_2)=D^*[\alpha\exp(\frac{r_e^*-r}{a})-\beta\exp(\frac{r_e^*-r}{2a})]\frac{q_1q_2}{d_1d_2} \quad (9)$$

where

$$D^*=D\frac{(4\sin h\frac{1}{2}Q_1\sin h\frac{1}{2}Q_2)^2}{Q_1Q_2\sin hQ_1\sin hQ_2}$$

$$\alpha=(1-Q_1\cot hQ_1)(1-Q_2\cot hQ_2)$$

$$\beta=2(1-\frac{Q_1}{2}\cot h\frac{Q_1}{2})(1-\frac{Q_2}{2}\coth\frac{Q_2}{2})$$

r_e^* is the new equilibrium distance.[7] The collision trajectory for the present system can be determined by solving the equation of motion written in the form

$$t=(\frac{1}{2}\mu)^{1/2}\int_{r_0}^{r}[E-\overline{U}_0(r)]^{-1/2}dr \quad (10)$$

where E is the relative kinetic energy and r_0 is the point of closest approach (t is taken to be zero at this point). For the potential function given by Eq.(8), the integration can be done analytically to give

$$\exp(\frac{r_e^*-r}{2a}) =\frac{E}{(ED^*+D^{*2})^{1/2}}\frac{1}{\cos h[(\frac{E}{2\mu})^{1/2}(\frac{t}{a})]-(\frac{D^*}{E+D^*})^{1/2}} \quad (11)$$

which transforms $U_{12}(r,q_1,q_2)$, given by Eq.(9), into the time-dependent perturbation energy $\overline{U}_{12}(t,q_1,q_2)$.

The Hamiltonian of the collision system for VV energy exchange is

$$H(t) =\frac{p_1^2}{2M_1}+\frac{p_2^2}{2M_2}+\frac{1}{2}M_1\omega_1^2q_1^2+\frac{1}{2}M_2\omega_2^2q_2^2+\overline{U}_{12}(t,q_1,q_2) \quad (12)$$

where p's are the momenta, ω's the angular frequencies, and M's the reduced masses. In terms of latter operators $(a_i^\dagger,a_i)$, Eq.(12) can be written as[7]

$$H(t)=\hbar\omega_1(a_1^\dagger a_1+\frac{1}{2})+\hbar\omega_2(a_2^\dagger a_2+\frac{1}{2}) +F(t)(a_1^\dagger a_2+a_1a_2^\dagger) \quad (13)$$

where

$$F(t)=\frac{1}{2}\hbar D^*d_1^{-1}d_2^{-1}(M_1M_2\omega_1\omega_2)^{-1/2}\{\alpha\exp[(r_e^*-r(t))/a] -\beta\exp[r_e^*-r(t))/2a]\}$$

, $a_1^\dagger a_2^\dagger$ and a_1a_2 are discarded because they represent the simultaneous excitation and de-excitation, respectively, of both oscillators. To formulate energy exchange probabilities, we now need to determine how the state of the interaction system change in time. In order to give the time development of the system and to describe processes which involve a change in the vibrational state, we require the state vector of the system $|\psi(t)>$ change in accordance with the Schrödinger equation of motion:

$$i\hbar|\dot{\psi}(t)>=H(t)|\psi(t)> \quad (14)$$

Then, according to Wei and Norman's Lie algebraic method,[9,10] we can express the solution of Eq.(14) for H(t) given by Eq.(13) as

$$|\psi(t)>=\{\prod_{j=1}^{n}\exp[g_j(t)H_j]\}|\psi(t_0)> \quad (15)$$

where g_j(t) are complex valued functions of time and H_j are constant operators. Thus, since the operators $a_1^\dagger a_2$, $a_1a_2^\dagger$, and $(a_1^\dagger a_1-a_2^\dagger a_2)$ form a closed system with respect to commutation, we look for the solution in the form $|\psi(t)>=c(t)\exp[g_1(t)a_1^\dagger a_2]\exp[g_2(g_2(t)a_1a_2^\dagger]\exp[g_3(t)(a_1^\dagger a_1-a_2^\dagger a_2)]|\psi(-\infty)>\equiv S(t)|\psi(-\infty)>$. $|\psi(t)>$ provides a complete description of the dynamics throughout the collision. Since the initial values of the functions are $g_1(-\infty)=g_2(-\infty)=g_3(-\infty)=0$ and $|c(-\infty)|=1$, when $|\psi(-\infty)>$ is specified, we can obtain a unique solution for $|\psi(t)>$ at all subsequent times through the transformation of $|\psi(-\infty)>$ by S(t). Thus the solution of Eq.(14) reduces to the determination of $c(t)$, $g_1(t)$, $g_2(t)$, and $g_3(t)$. Once these functions are determined VV energy exchange probabilities can be calculated from the expression

$$P_{v_1v_2}^{v'_1v'_2}=\lim_{t\to\infty}|<v_1'v_2'|S(t)|v_1v_2>|^2 \quad (16)$$

Introducing $|\psi(t)>$ into the wave equation, setting the coefficients of the operators $a_1^\dagger a_2$, $a_1a_2^\dagger$, and $a_1^\dagger a_1-a_2^\dagger a_2$ equal to zero, we obtain the following differential equations:[11]

$$\dot{c}(t)/c(t)=-\frac{1}{2}i(\omega_1+\omega_2)$$

$$i\hbar\dot{g}_1(t)+\Delta Eg_1(t)+F(t)g_1^2(t)-F(t)=0$$

$$i\hbar\dot{g}_2(t)-\Delta Eg_2(t)-2F(t)g_1(t)g_2(t)-F(t)=0$$

$$i\hbar\dot{g}_3(t)-F(t)g_1(t)-\frac{1}{2}\Delta E=0$$

For an arbitrary form of F(t), analytical forms of the solutions cannot be obtained, but the differential equations appear in simple forms, so that application of the Runge-kutta method,[12] for example, is straightforward. The general form of the VV energy exchange probability for $v_1v_2\rightarrow v_1'v_2'$ can be written, taking $|\psi(-\infty)\rangle=|v_1v_2\rangle$, as[11,13-14]

$$P_{v_1v_2}^{v_1'v_2'}(E)=\frac{v_1'!v_2'!}{v_1!v_2!}|\exp[(v_1-v_2)g_3(\infty)]|^2|g_2(\infty)|^{2(v_1'-v_1)}$$

$$\times[\sum_{m=0}^{v_2'}\frac{[g_1(\infty)g_2(\infty)]^m(v_1'+m)!}{m!(v_1'-v_1+m)!(v_2'-m)!}]^2 \qquad (18)$$

for $v_1'>v_1$ and $v_1'>v_2$. For $v_1'<v_1$, we must interchange v_2 and v_2', as well as $g_1(\infty)$ and $g_2(\infty)$, which are not equal to each other. For the present 1,0→0,1 VV energy exchange system,

$$P_{10}^{01}(E)=|\exp[-g_3(\infty)]|^2|g_2(\infty)|^2 \qquad (19)$$

We shall replace E in $P_{10}^{01}(E)$ by the symmetrized energy $E_2=\frac{1}{4}[E_i^{1/2}+E_f^{1/2}]$. To complete the formulation of the energy transfer probability expression we must include the effects of nonzero impact parameter(b) collisions. An approach of including these effects is to replace E by $E(1-b^2/r^{*2})$, i.e., we now have $P_{10}^{01}(E,b)$. Here r* is a characteristic distance which can be defined as the hard-sphere collision diameter. With these considerations we write the thermal-average probability

$$P_{10}^{01}(T)=\frac{1}{(kT)^2\pi r^{*2}}\int_0^{r^*}\int_0^{\infty}2\pi b\,E\,P_{10}^{01}(E,b)dEdb \qquad (20)$$

The integration will be carried out by use of Simpson's 1/3 rule on a IBM computer. We converted the calculated values of $P_{10}^{01}(T)$ to the rate constants as[15]

$$k_{10}^{01}(T)=Z\,P_{10}^{01}(T)$$

$$=2.753\times10^{12}r^{*2}\left(\frac{T}{\mu}\right)^{1/2}P_{10}^{01}(T)\quad \text{cm}^3/\text{mol-sec}$$

$$=4.571\times10^{-12}r^{*2}\left(\frac{T}{\mu}\right)^{1/2}P_{10}^{01}(T)\ \text{cm}^3/\text{molecule-sec} \qquad (21)$$

where μ is the reduced mass in amu and r* in Å. Here the rate constants have been converted from probabilities for energy exchange by multiplying by the hard sphere collision frequency. The hard sphere diameter was obtained from Hirschfelder et al.[16] This simple calculation applies only if the gases are perfect. Gas imperfections lead to collisional frequencies at low temperatures being somewhat higher than those for a perfect gas.

Results and Discussion

In this work we have calculated rotationally averaged rate constants for nonresonant VV energy transfer process, i.e., $N_2(v=1)+O_2(v=0)\rightarrow N_2(v=0)+O_2(v=1)$ system. To calculate rate constants, we use[16,17] D = 95.66k and $a^{-1}=4.75$Å^{-1}. The energy level spacings and the value of the energy mismatch ΔE are determined using spectroscopic constants from Mizushima.[18] The calculated rate constants are shown in Figure 1 together with the experimental data of Gregory et al.[1] and Maricq *et al.*[2] over the temperature range 90-300K; the calculation is extended to temperatures below 90K. This extension to lower temperatures is intended to show predictions of the gas-phase model, but $k^{gas}(T)\neq k^{liq}(T)$ so the calculation at such temperatures may not be physically meaningful. However, gas-phase rate constants calculated from the isolated binary collision model is known to be smaller than liquid-phase values by a factor of about 5 due to the change in the collision frequency.[19,20] Thus useful information on the liquid-phase rates can be extracted from such calculations. In Fig. 1 we notice that the present results are in reasonable agreement with the experimental. However, near 300K the former overestimates the latter. This trend is similar to Maricq *et al.*[2]

Among the terms discarded from Eq.(2) in deriving $P_{10}^{01}(E)$ are $q_i(\partial U/\partial q_i)\equiv G_i(t)(a_i^{\dagger}+a_i)$, which cause pure VT transitions. However, they can affect the VV process at high collision energies through the VT steps AB(v = 1)→AB(v = 0) and CD(v = 0)→CD(v = 1); in each of these "half" steps, the energy $\hbar\omega$ is either absorbed or released by the translational motion, but the combined process is still the VV process, *i.e.*, in the present case $N_2(v=1)+O_2(v=0)\rightarrow N_2(v=0)+O_2(V=1)$. Such VT steps are very inefficient and do not affect the VV process at low collision energies, but at energies several times $\hbar\omega$, they can become strongly coupled with the pure VV process. We also note that the second-order derivatives in Eq.(2), $\frac{1}{2}q_i^2(\partial^2U/\partial q_i^2)\equiv K_i(t)(a_i^{\dagger}+a_i)^2$, are not only responsible for two-quantum processes but also for time-dependent frequen-

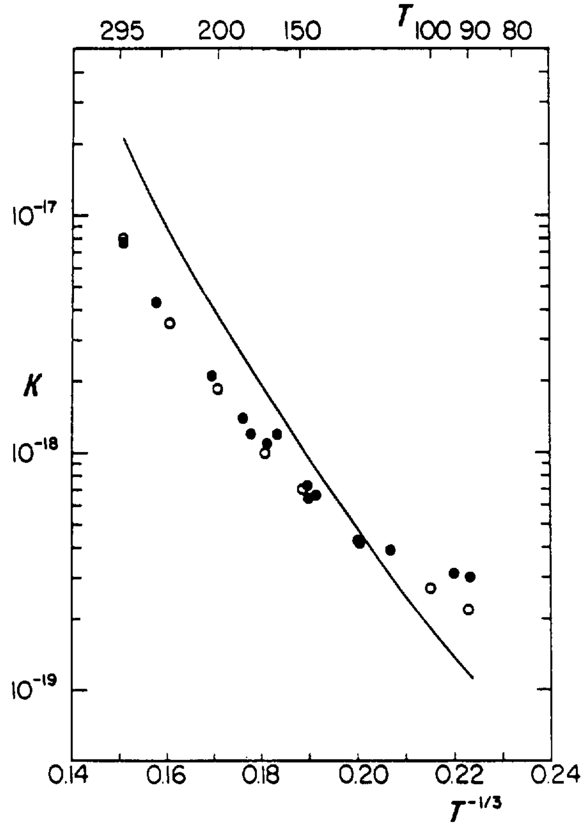

Figure 1. Plot of rate constant vs temperature. The solid curve is obtained from Eq.(21). Experimental data are taken from: ● Ref. 1; ○ Ref. 2.

cy corrections. Therefore, we now write the Hamiltonian for the VV–VT process in the term[21]

$$H=H^0+H^{VV,VT}=[h\omega_1+2K_1(t)](a_1^\dagger a_1+\frac{1}{2})$$
$$+[h\omega_2+2K_2(t)](a_2^\dagger a_2+\frac{1}{2})+G_1(t)(a_1^\dagger+a_1)$$
$$+G_2(t)(a_2^\dagger+a_2)+F(t)(a_1^\dagger a_2+a_1 a_2^\dagger) \qquad (22)$$

and look for the solution of Eq.(14) in the form

$$|\psi(t)>^{VV,VT}$$
$$=c(t)\exp[g_1(t)a_1a_2^\dagger]\exp[g_2(t)a_1^\dagger a_2]\exp[g_3(t)(a_1^\dagger a_1-a_2^\dagger a_2)]$$
$$\times\exp[g_4(t)a_1^\dagger]\exp[g_5(t)a_1]\exp[g_6(t)a_2^\dagger]\exp[g_7(t)a_2]|\psi(t_0)>$$
$$\equiv S^{VV,VT}(t)|v_1v_2> \qquad (23)$$

After substituting these two expressions in Eq.(14), we set the coefficient of each operator or operator product equal to zero to obtain, in addition to the equation for $g_1(t)$, $g_2(t)$ and $g_3(t)$ already given Chap. 2 for the pure VV case, the following differential equations:

$$\dot{c}(t)/c(t)=-\frac{1}{2}i(\omega_1+\omega_2)-i\hbar^{-1}[G_1(t)g_4(t)+G_2(t)\ g_6(t)]$$
$$-i\hbar^{-1}[K_1(t)+K_2(t)]$$
$$\dot{g}_4(t)+i[\omega_1+2\hbar^{-1}K_1(t)]g_4(t)+i\hbar^{-1}F(t)g_6(t)=-i\hbar^{-1}G_1(t)$$
$$\dot{g}_5(t)-i[\omega_1+2\hbar^{-1}K_1(t)]g_5(t)-i\hbar^{-1}F(t)g_7(t)=-i\hbar^{-1}G_1(t)$$
$$\dot{g}_6(t)+i[\omega_2+2\hbar^{-1}K_2(t)]g_6(t)+i\hbar^{-1}F(t)g_4(t)=-i\hbar^{-1}G_2(t)$$
$$\dot{g}_7(t)-i[\omega_2+2\hbar^{-1}K_2(t)]g_7(t)-i\hbar^{-1}F(t)g_5(t)=-i\hbar^{-1}G_2(t) \qquad (24)$$

The initial conditions are $g_4(-\infty)=g_5(-\infty)=g_6(-\infty)=g_7(-\infty)=0$ and $|c(-\infty)|=1$. Here, the coefficients of a_1^+, a_1, a_2^+, and a_2 produced the differential equations in $g_4(t)$, $g_5(t)$, $g_6(t)$, and $g_7(t)$, respectively; terms independent of these operators led to the equation of $c(t)$.

From the substitution of Eq.(23) in (16) and followed by exponential operations of $|v_1v_2>$, we obtain, after lengthy but straightforward applications of commutation relations, the VV–VT probability for $v_1v_2 \rightarrow v_1'v_2'$ as

$$P_{v_1v_2}^{v_1'v_2'}=\lim_{t\to\infty}\left\{\frac{v_1'!\ v_2'!\ v_2!}{v_1!}|c(t)|^2|\exp g_3(t)(v_1-v_2)|^2\right.$$
$$\times\left|\sum_{n=0}^{v_1'}\sum_{p=0}^{v_2'}\sum_{r=0}^{v_1+s}\sum_{s=0}^{v_2}\frac{[g_4(t)g_5(t)]^n[g_6(t)g_7(t)]^p[g_1(t)]^r[g_2(t)]^s}{n!\ (v_1+s-r-v_1'+n)!\ p!\ (v_2-s+r-v_2'+p)!}\right.$$
$$\left.\left.\times\frac{[g_5(t)]^{v_1+s-r-v_1'}[g_7(t)]^{v_2-s+r-v_2'}(v_2-s+r)!\ (v_1+s)!}{r!\ s!\ (v_1'-n)!\ (v_2'-p)!\ (v_2-s)!}\right|^2\right\} \qquad (25)$$

For the present 10→01 process,

$$P_{10}^{01}$$
$$=|c(t)|^2|\exp[g_3(t)]|^2|g_1(t)[1+g_6(t)g_7(t)]+g_5(t)g_6(t)|^2 \qquad (26)$$

In similar to $g_1(t)$, $g_2(t)$ and $g_3(t)$, the numerical solutions of $g_4(t)$, $g_5(5)$, $g_6(t)$ and $g_7(t)$ can be also obtained. Once the solutions are found, the VV–VT transition probability for 10→01 process can be determined from Eq.(26). In the computations, the integration range and the number of steps were adjusted until changing them no longer affected the results. For each value of E, we found choosing the integration range from $\tau=(E/2\mu)^{1/2}t/a=-10$ to 10 and the integration steps of 700 satisfied this condition. Calculated values of VV–VT energy exchange rate constants are plotted in Figure 2 with the pure VV results as a function of a temperature. This figure shows that the VV–VT energy exchange rate constants are smaller than the pure VV results by a factor of ~2. For example, at 295K, $k(T)^{VV}=2.1\times10^{-17}$cc/molecule-sec, whereas $k(T)^{VV\text{-}VT}=1.0\times10^{-17}$cc/molecule-sec, which is very close to the observed value[2] of 0.8×10^{-17}. At 91*K*, there is an important study of liquid system by Chandler and Ewing[22] giving $k(T)=1.2\pm0.9\times10^{-19}$cc/molecule-sec. At this temperature, VV–VT energy exchange rate constant is 6.3×10^{-20}cc/molecule-sec. When this value is multiplied by 5, the result(~3.0×10^{-19}cc/molecule-sec) is larger than the measured rate constant by only a factor of 2.5.

On the other hand, for the present VV energy exchange process, the energy mismatch is 773cm^{-1}, which is to be contrasted with the rotational energy spacing. Each of the molecules N_2 and O_2 has a rotational constant of ≃2cm^{-1}. Therefore, at 295K the rotational state most likely populated is J = 7, while at 90K it is J = 4. The rotational energy spacing to states adjacent to J = 7 is ≃30cm^{-1}, and to states adjacent to J = 4 the spacing is 15cm^{-1}. Counting simultaneous changes of $\Delta J=1$ in both of the colliding molecules leads to a maximum change in the rotational energy of ≃60cm^{-1}. This is ~10% of the vibrational energy defect. When the simultaneous changes of the rotational energy is considered, the predicted VV–VT

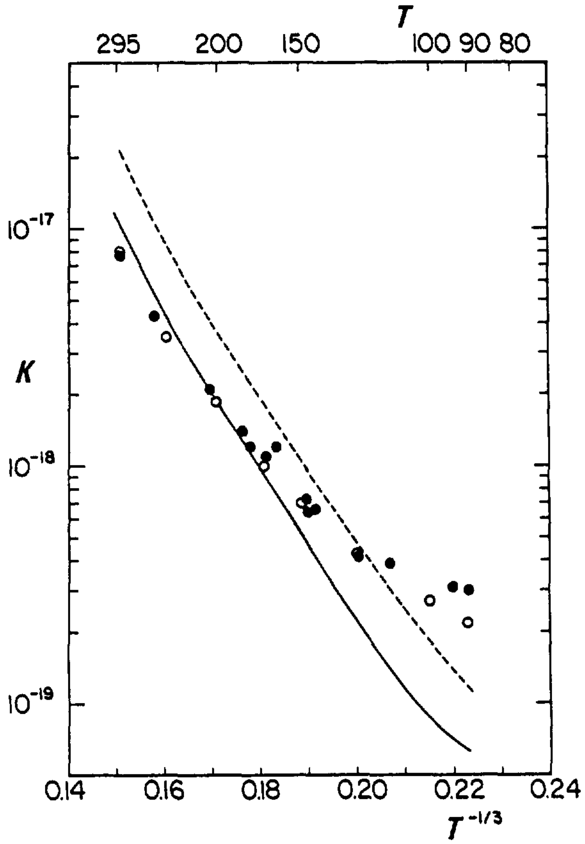

Figure 2. Plot of $k(T)$ vs $T^{-1/3}$. The solid curve is for the VV–VT and the broken curve for the pure VV. Experimental data are taken from: ● Ref. 1; ○ Ref. 2.

rate constants are increased by a factor of ~2 in the considered temperature range. For example, at 295K, $k(T)=1.0\times10^{-17}$ cc/molecule-sec for no-consideration of the simultaneous changes of the rotational energy, while $k(T)=2.0\times10^{-17}$ cc/molecule-sec for consideration. At 91K, $k(T)=6.3\times10^{-20}$ cc/molecule-sec for the former and $k(T)=9.4\times10^{-20}$cc/molecule-sec for the latter.

The energy transfer probabilities are converted into the rate constants by multiplying them by an average hard sphere collision frequency using collision diameter taken from Hirschfelder *et al.*[16] In fact it is a simplification to use such a collision frequency because both the magnitude of the velocities effective in causing energy transfer and the frequencies of those collisions depend upon several factors. This includes not only the frequencies of the vibrations involved and the steepness of the intermolecular repulsive potential, but also an attractive forces and the masses of the colliding species. When the collision frequency correction of about 5 is introduced, the VV-VT calculation appears to give rate constant which is consistent with the available experimental value in the liquid phase. Until a successful liquid-phase theory capable of producing accurate rate constant is developed, we therefore suggest that gas-phase models like the present one can serve as a physical guide to researchers in this field.

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