The AS with β-carotene incorporated into the hydrophobic bilayer of phospholipid (DMPC or DMPC/PEA) resulted in the photosensitized reduction of MV^{2+} with less efficiency than AC-incorporated into the outer hydrophilic layer, but preventing the reverse reaction of electron transfer more effectively than the latter system. Also DMPC or PEA liposomes were observed to be more stable than any other phospholipid-liposomes. Thus, application of the model system, AS-β-carotene-DMPC appears to be feasible for the reduction of water to hydrogen in the presence of a certain catalyst, because the transient photoproducts (e.g., MV^+) of electron-transfer reaction are stable engough to efficiently react with H_2O.

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Effects of Molecular Attraction and Orientations in the Vibration-Vibration Energy Exchange

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The effects of molecular attraction and orientations for the energy mismatch variance, vibrational energy level and double-quantum transition, in the vibration-vibration energy exchange, have been considered. The contribution of molecular attraction increases the exchange rate of the purely repulsive interaction, in general, significantly, but which becomes smaller as the temperature is increased. As the energy mismatch is increased, its contribution is also increased, but which is small. However, its contribution for the double-quantum transition is very paramount. At each orientation, the exchange rate constants have been calculated and compared with the results for rotational average, and it is found that the exchange rate is a strong function of the orientation angles of colliding molecules. We have also discussed about the system having the strong interaction such as the hydrogen bond, and it is found that for this system the preferred orientation should be considered in order to calculate the exchange rates.

Introduction

The molecular attraction plays a crucial role in the vibration-vibration(VV) energy transfer.[1] In particular, if there is a strong attraction, its importance is very significant.[2-6] As colliding molecules approach each other, if they are not symmetric thus cannot freely rotate, they must interact with the preferred orientation.[7,8] But, if they are almost symmetric, there is no reason having the preferred orientation, so the colliding molecules can freely rotate during the interaction. Such motions can seriously affect the magnitude of the overall interaction potential, thus influencing the processes of intermolecular VV energy exchange. Therefore, it is important to consider the effects of molecular orientation on vibrational

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energy transfer.

This paper treats these effects of molecular attraction and orientations, in particular, for the energy mismatch variance, vibrational energy level and double-quantum transition in the VV energy exchange. To treat these problems, we shall consider the vibrational energy exchange rate constants at different molecular orientations using a Morse-type interaction potential. On the other hand, to examine the effect of the preferred orientation, we shall consider the system having the strong attraction such as hydrogen bond. Energy exchange rate constants will be formulated by solving the time-dependent Schrödinger equation of the interaction system for the evolution operator,[10] which transforms the initial state $|\psi(t_0)\rangle$ of the interaction system into some final state at time $t, |\psi(t)\rangle$. To show the temperature dependence of these effects, we shall carry out calculations over a temperature range of 100–3000K.

Interaction Potentials

For the interaction of a diatomic molecules AB and CD, we shall assume the potential energy as a Morse type composed of four atom-atom interactions.[9] That is,

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

where $U(r_i) = D\{\exp[(r_{ie} - r_i)/a] - 2\exp[(r_{ie} - r_i)/2a]\} = U_{rep} + U_{att}$. $U_{rep} = D\exp[(r_{ie} - r_i)/a]$, $U_{att} = -2D[(r_{ie} - r_i)/2a]$, D and a are potential parameters, r_i's are the distances between atoms; $i = 1$ or 2 represents the A⋯C or A⋯D interaction, and $i = 3$ or 4 the B⋯C or B⋯D. These distances can then be approximated by $r_1 = r - \gamma_1(d_1 + q_1)\cos\theta_1 + \gamma_3(d_2 + q_2)\cos\theta_2$ and $r_2 = r - \gamma_1(d_1 + q_1)\cos\theta_1 - \gamma_4(d_2 + q_2)\cos\theta_2$, $r_3 = r + \gamma_2(d_1 + q_1)\cos\theta_1 + \gamma_3(d_2 + q_2)\cos\theta_2$ and $r_4 = r + \gamma_2(d_1 + q_1)\cos\theta_1 - \gamma_4(d_2 + q_2)\cos\theta_2$. Here, r is the relative separation between molecules 1 and 2 and the equilibrium distances, r_{ie}'s can be obtained by setting $q_1 = q_2 = 0$, $\theta_1 = \theta_{1e}$, and $\theta_2 = \theta_{2e}$, where θ_{ie}'s are taken as the orientation angles at which $U(r_i)$'s are minima. Here, q_i is the vibrational coordinate of the ith molecule, d_i its equilibrium value, θ_i measures the orientation of it with respect to r, $\gamma_{1,2} = m_{B,A}/(m_A + m_B)$ and $\gamma_{3,4} = m_{D,C}/(m_C + m_D)$. Introducing these distances into eq.(1) and expanding $\exp(\gamma_i q_i/a) = 1 + (\gamma_i/a)q_i$, we take the repulsive part of eq.(1) in the form

$$U_{rep} = \frac{1}{4}D \, \exp[(r_{ie} - r_e)/a] \, \{f_0 \exp[(r_e - r)/a]$$

$$+ f_1 \exp[(r_e - r)/a] (q_1/a)\cos\theta_1$$

$$+ f_2 \exp[(r_e - r)/a] (q_2/a)\cos\theta_2$$

$$+ f_{12} \exp[(r_e - r)/a] (q_1 q_2/a^2)\cos\theta_1\cos\theta_2\}$$

where, the angle-dependent functions are

$$f_0 = e^{(Q_1 - Q_3)} + e^{(Q_1 + Q_4)} + e^{(-Q_2 - Q_3)} + e^{(-Q_2 + Q_4)}$$

$$f_1 = \gamma_1 [e^{(Q_1 - Q_3)} + e^{(Q_1 + Q_4)}] - \gamma_2 [e^{(-Q_2 - Q_3)} + e^{(-Q_2 + Q_4)}]$$

$$f_2 = -\gamma_3 [e^{(Q_1 - Q_3)} + e^{(Q_1 + Q_4)}] + \gamma_4 [e^{(-Q_2 - Q_3)} + e^{(-Q_2 + Q_4)}]$$

$$f_{12} = -\gamma_1\gamma_3 e^{(Q_1 - Q_3)} + \gamma_1\gamma_4 e^{(Q_1 + Q_4)} + \gamma_2\gamma_3 e^{(-Q_2 - Q_3)} - \gamma_2\gamma_4 e^{(-Q_2 + Q_4)}$$

with $Q_{1,2} = \gamma_i d_1 \cos\theta_1/a$ and $Q_{3,4} = \gamma_i d_2\cos\theta_2/a$. We can, then, take the attractive part as follows:

$$U_{att} = -\frac{1}{2}D \, \exp[(r_{ie} - r_e)/2a] \, \{g_0 \exp[(r_e - r)/2a]$$

$$+ g_1 \exp[(r_e - r)/2a] (q_1/2a)\cos\theta_1$$

$$+ g_2 \exp[(r_e - r)/2a] (q_2/2a)\cos\theta_2$$

$$+ g_{12} \exp[(r_e - r)/2a] (q_1 q_2/4a^2)\cos\theta_1\cos\theta_2\} \qquad (3)$$

where,

$$g_0 = e^{(Q_1 - Q_3)/2} + e^{(Q_1 + Q_4)/2} + e^{(-Q_2 - Q_3)/2} + e^{(-Q_2 + Q_4)/2}$$

$$g_1 = \gamma_1 [e^{(Q_1 - Q_3)/2} + e^{(Q_1 + Q_4)/2}] - \gamma_2 [e^{(-Q_2 - Q_3)/2} + e^{(-Q_2 + Q_4)/2}]$$

$$g_2 = -\gamma_3 [e^{(Q_1 - Q_3)/2} + e^{(Q_1 + Q_4)/2}] + \gamma_4 [e^{(-Q_2 - Q_3)/2} + e^{(-Q_2 + Q_4)/2}]$$

$$g_{12} = -\gamma_1\gamma_3 e^{(Q_1 - Q_3)/2} + \gamma_1\gamma_4 e^{(Q_1 + Q_4)/2} + \gamma_2\gamma_3 e^{(-Q_1 - Q_3)/2} - \gamma_2\gamma_4 e^{(-Q_1 + Q_4)/2}.$$

Combining eqs.(2) and (3), we finally obtain the overall interaction energy by

$$U(r, q_1, q_2, \theta_1, \theta_2) = U_{rep} + U_{att} = U_0(r, \theta_1, \theta_2)$$

$$+ U_1(r, q_1, \theta_1, \theta_2) + U_2(r, q_2, \theta_1, \theta_2) + U_{12}(r, q_1, q_2, \theta_1, \theta_2) \cdot$$
$$(4)$$

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

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

In the formulation of U_0 and U_{12}, the quantities $\exp[(r_{ie} - r_e)/a]$ and $\exp[(r_{ie} - r_e)/2a]$ appear as shown above, we shall take $r_{ie} - r_e = -(d_1 + d_2)/2a$ or $\exp[(r_{ie} - r_e)/a] = \exp[-(d_1 + d_2)/2a]$.

The collision trajectory for the present system can be determined by solving the equation of motion written in the form

$$t = (\frac{1}{2}\mu)^{\frac{1}{2}} \int_{r_0}^{r} [E - \bar{U}_0(r)]^{-\frac{1}{2}} dr.$$

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 described by $U_0(r,\theta_1,\theta_2)$, the integration can be done analytically to give

$$\exp(\frac{r_e - r}{2a}) = \frac{E}{(EJ + K^2)^{\frac{1}{2}} \{\cosh[(\frac{E}{2\mu})^{\frac{1}{2}}(\frac{t}{a})] - \frac{K}{(EJ + K^2)^{\frac{1}{2}}}\}} \quad (6)$$

where, $J = \frac{1}{4}Df_0\exp[-(d_1 + d_2)/2a]$, $K = \frac{1}{4}Dg_0\exp[-(d_1 + d_2)/4a]$. Using this expression, we can then convert $U_{12}(r,q_1,q_2,\theta_1,\theta_2)$ into $U_{12}(t,q_1,q_2,\theta_1,\theta_2)$.

Energy Exchange Rate Constants

The Hamiltonian of the collision system for VV energy exchange at different orientation is

$$H(t) = \frac{1}{2}M_1^{-1}p_1^2 + \frac{1}{2}M_2^{-1}p_2^2 + \frac{1}{2}M_1\omega_1^2 q_1^2 + \frac{1}{2}M_2\omega_2^2 q_2^2$$

$$+ U_{12}(t, q_1, q_2, \theta_1, \theta_2) \qquad (7)$$

which, in terms of ladder operators $(a_i^\dagger, a_i)$, can be written as

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

$$+ F(t, \theta_1, \theta_2)(a_1^\dagger a_2^\dagger + a_1^\dagger a_2 + a_1 a_2^\dagger + a_1 a_2) = H^\circ + H'(t) \quad (8)$$

where, $F(t) = \frac{1}{2}\hbar a^{-2}D(M_1 M_2\omega_1\omega_2)^{-\frac{1}{2}}\{\alpha\exp[(r_e - r)/a] - \beta\exp[(r_e - r)/2a]\}\cos\theta_1\cos\theta_2$, $\alpha = \frac{1}{4}f_{12}\exp[-(d_1 + d_2)/2a]$ and $\beta = \frac{1}{2}g_{12}\exp\{-(d_1 + d_2)/4a]$. Here $a_1^\dagger a_2^\dagger$ and $a_1 a_2$ represent the

simultaneous excitation and de-excitation, respectively, of both molecules, so they will be discarded from the present study of VV energy exchange processes. To formulate energy exchange probabilities, we now need to determine how the state of the interaction system changes 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 $|\psi(t)\rangle$ change in accordance with the Schrödinger equation of motion:

$$i\hbar |\dot{\psi}(t)\rangle = H(t) |\psi(t)\rangle \cdot \tag{9}$$

To solve this equation, we look for a solution to the form

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle, \tag{10}$$

where $U(t, t_0)$ is a time evolution operator satisfying the equation

$$i\hbar \dot{U}(t, t_0) = H(t)U(t, t_0) \tag{11}$$

with the initial condition $U(t_0, t_0) = 1$. Equation (10) is of fundamental importance to energy exchange problems, because it describes the evolution of the unperturbed initial state $|\psi(t_0)\rangle$ after the perturbation is applied. Once this solution is found, the probability of finding any particular final state $|v_1', v_2'\rangle$ after the collision can then be expressed in the form

$$P_{v_1 v_2}^{v_1' v_2'} = \lim_{t \to \infty} |\langle v_1' v_2' | \psi(t)\rangle|^2 = \lim_{t \to \infty} |\langle v_1' v_2' | U(t, t_0) |v_1 v_2\rangle|^2 \tag{12}$$

where the initial state is $|\psi(t_0)\rangle = |v_1 v_2\rangle$. The state vector $|\psi(t)\rangle$ provides a complete description of the dynamics throughout the collision. According to Ref. 10, the evolution operator becomes

$$U(t, t_0) = \exp\left(-\frac{iH^0 t}{\hbar}\right) T \exp\left[-\frac{i}{\hbar} \int_{t_0}^{t} \tilde{H}'(t)dt'\right] \tag{13}$$

Here T stands for the time ordered product, and $\tilde{H}'(t) = F(t, \theta_1, \theta_2)\{a_1^\dagger a_2 \exp[i(\omega_1 - \omega_2)t] + a_1 a_2^\dagger \exp[-i(\omega_1 - \omega_2)t]\}$. Then, if $\Delta\omega = \omega_1 - \omega_2$, from eqs. (10) and (13), we have

$$|\psi(t)\rangle = \exp\left(-\frac{iH^0 t}{\hbar}\right) T \exp\left\{-\frac{i}{\hbar}\left[\int_{t_0}^{t} F(t', \theta_1, \theta_2)\exp(i\Delta\omega t')dt' a_1^\dagger a_2 + \int_{t_0}^{t} F(t', \theta_1, \theta_2)\exp(-i\Delta\omega t')dt' a_1 a_2^\dagger\right]\right\} |\psi(t_0)\rangle \cdot \tag{14}$$

If we take $t_0 = -\infty$ and a measurement is made at a sufficiently long time later($t \to \infty$), from eq.(12), the probability of transition from $|v_1 v_2\rangle$ to $|v_1' v_2'\rangle$ is

$$P_{v_1 v_2}^{v_1' v_2'}(E) = |\langle v_1' v_2' | T \exp\left(-\frac{i}{\hbar} \int_{-\infty}^{\infty} F(t, \theta_1, \theta_2)\exp(i\Delta\omega t)dt \times (a_1^\dagger a_2 + a_1 a_2^\dagger)\right) |v_1 v_2\rangle|^2 \tag{15}$$

The value of the integral is found by contour integration to be

$$\frac{i}{\hbar} \int_{-\infty}^{\infty} F(t, \theta_1, \theta_2)\exp(i\Delta\omega t)dt = \frac{2\pi\mu\Delta\omega D}{J(M_1 M_2 \omega_1 \omega_2)^{\frac{1}{2}}}$$

$$\{a \cos h [(\frac{2\mu}{E})^{\frac{1}{2}} a\Delta\omega (\pi - b)] + \frac{1}{\Delta\omega a} (\frac{J}{2\mu})^{\frac{1}{2}} (\frac{K}{J} a - \beta)$$

$$\sin h [(\frac{2\mu}{E})^{\frac{1}{2}} a\Delta\omega (\pi - b)]\} \csc h [(\frac{2\mu}{E})^{\frac{1}{2}} a\Delta\omega \pi]$$

$$\times \cos \theta_1 \cos \theta_2 \equiv G(E, \theta_1, \theta_2), \tag{16}$$

where $b = \cos^{-1}[(\frac{K^2}{K^2 + EJ})^{\frac{1}{2}}]$. Because of the time ordering,

explicit forms of probabilities cannot be obtained for the present system. According to the Ref. 11, however, the removal of the time ordering operator leads to an explicit expression, we shall write the probability in the form

$$P_{v_1 v_2}^{v_1' v_2'}(E, \theta_1, \theta_2) = |\langle v_1 v_2 | \exp\{-iG(E, \theta_1, \theta_2)(a_1^\dagger a_2 + a_1 a_2^\dagger)\} |v_1 v_2\rangle|^2 \cdot \tag{17}$$

Then, after lengthy but straightforward operations by expanding

$$\exp[-iG(a_1^\dagger a_2 + a_1 a_2^\dagger)] = 1 - iG(a_1^\dagger a_2 + a_1 a_2^\dagger) - G^2(a_1^\dagger a_2 + a_1 a_2^\dagger)^2 + iG^3(a_1^\dagger a_2 + a_1 a_2^\dagger)^3 + G^4(a_1^\dagger a_2 + a_1 a_2^\dagger)^4 - iG^5(a_1^\dagger a_2 + a_1 a_2^\dagger)^5 + \cdots,$$

and using the relation $a^\dagger |v\rangle = \sqrt{v+1}|v+1\rangle$, $a|v\rangle = \sqrt{v}|v-1\rangle$ we obtain

$$P_{v_2, 0}^{v_1 - n, n}(E, \theta_1, \theta_2) = \frac{v_1!}{(v_1 - n)!n!} \sin^{2n}G \cos^{2(v_1 - n)}G \cdot \tag{18}$$

We shall replace E in $P_{v_1 v_2}^{v_1' v_2'}(E)$ by the symmetrized energy $E_s = \frac{1}{4}[E_i^{\frac{1}{2}} + E_f^{\frac{1}{2}}]^2$, i.e., $E_s = \frac{1}{4}[(E \pm \Delta E)^{\frac{1}{2}} + E^{\frac{1}{2}}]^2$, where + for the exothermic case and - for the endothermic case. We shall introduce the impact parameter b in the probability expression as $E(1 - b^2/r^{*2})$, where r^* is a constant distance chosen in the most important region of energy exchange. With the introduction of the energy symmetrization and impact parameter, we define the average of $P_{v_1 v_2}^{v_1' v_2'}(E, \theta_1, \theta_2, b)$ over E, b, θ_1 and θ_2 as

$$P_{v_1 v_2}^{v_1' v_2'}(T) = \frac{1}{4\pi r^{*2}(kT)^2} \int_0^\pi \sin \theta_1 d\theta_1 \int_0^\pi \sin \theta_2 d\theta_2$$

$$\int_0^{r^*} 2\pi b \, db \int_0^\infty E \, P_{v_1 v_2}^{v_1' v_2'}(E, \theta_1, \theta_2, b)$$

$$\exp(-E/kT)dE \tag{19}$$

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(T) to the rate constants[12] as

$$k_{v_1 v_2}^{v_1' v_2'}(T) = Z \, P_{v_1 v_2}^{v_1' v_2'}(T)$$

$$= 2.753 \times 10^{12} \, r^{*2} (\frac{T}{\mu})^{\frac{1}{2}} \, P_{v_1 v_2}^{v_1' v_2'}(T) \quad \text{cm}^3/\text{mol-sec}$$

$$= 4.5708 \times 10^{-12} \, r^{*2} (\frac{T}{\mu})^{\frac{1}{2}} \, P_{v_1 v_2}^{v_1' v_2'}(T) \quad \text{cm}^3/\text{molecule-sec}, \tag{20}$$

where μ is the reduced mass in amu.

Results and Discussion

For numerical illustration, we have taken $N_2(v) + O_2(0) \rightarrow N_2(v-1) + O_2(1)$ system. To calculate energy exchange rate constants, we use[13,14] D = 91.5k and a^{-1} = 4.75Å^{-1}. The energy level spacings and the values of the energy mismatch ΔE are determined using spectroscopic constants from Mizushima.[15] Using these values we first analyze the temperature dependence of the VV energy exchange rate constants for N_2 $(v = 1) + O_2(v = 0) \rightarrow N_2(v = 0) + O_2(v = 1)$ in the range of 90 – 300K, which is shown in Figure 1. This figure shows that the VV energy exchange rate constants calculated from the Morse potential are significantly greater than those calculated using only the repulsive part of the potential. For example, at 295K, the rate constants are 2.136×10^{-17} and 6.046×10^{-18}, respectivey. That is, at this temperature, the contribution of
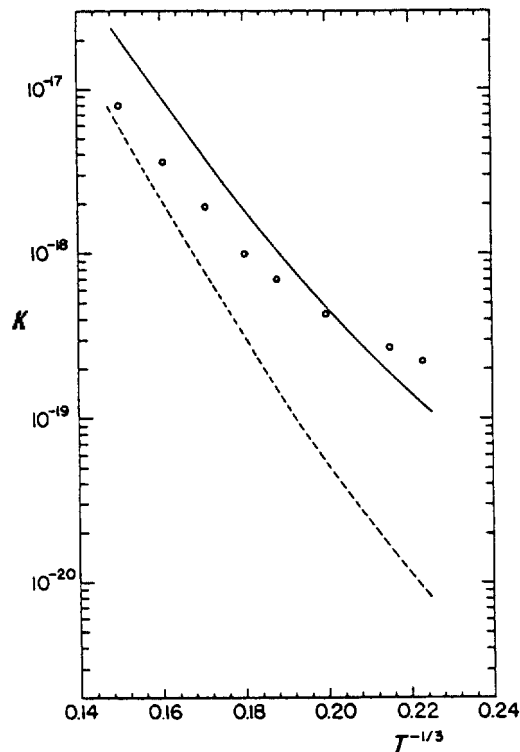
Figure 1. Temperature dependence of the VV energy exchange rate constant for $N_2(1)+O_2(0)\rightarrow N_2(0)+O_2(1)$ in the range 90-300K. The solid curve represents the rate constants calculated from the Morse potential; the broken curve is from the purely repulsive interaction.

Figure 2. Dependence of the VV energy exchange rate constant for $N_2(v)+O_2(0)\rightarrow N_2(v-1)+O_2(1)$ on v at 295K. The solid curve is calculated from the Morse potential and the broken curve is from the purely repulsive interaction.

moecular attraction increases the predicted rate constant of the purely repulsive interaction by a factor 3.5; at 100K the effect is much greater(a factor as large as 11.7). This increase does not stem primarily from the attractive forces accelerating the two colliding particles toward each other, but instead from the difference in the shapes of the potentials at low energies. Though the Morse potential decreases exponentially with r at very small distances, at distances approaching the potential minimum, the rate of decrease is more rapid than exponential. This is based on the assumption that the dominant contribution to the integral eq.(16) comes from the region of the classical turning point.[16] Assuming that the colliding molecules approach along the z axis of our coordinate frame, the description in section I,$r_i \rightarrow r-(d_1+q_1)|\cos\theta_1|-(d_2+q_2)|\cos\theta_2|$ supposes that the change in potential energy due to a change in bond length varies as the projection of the bond axis along the collision axis. $F(t)$ in eq.(16) can be also written in the form $F(t)= \frac{1}{2}\hbar(M_1M_2\omega_1\omega_2)^{-\frac{1}{2}}(\partial^2 U/\partial q_1\partial q_2)^{\prime\prime}$, so the integral Eq.(16) is dependent on the steepness in the turning point. At low collision energies, the potential near the classical turning point is steeper for the Morse potential than for the exponential repulsive potential alone. This provides a more sudden collision and thereby leads to a larger rate constant. At 3000K, however, the molecular attraction increases the predicted rate constant of the purely repulsive part of the potential by a factor 1.35 at best. As the temperature is increased, the average collision energy is increased significantly, thus the contribution of molecular attraction is decreased.

For two-quantum exchange $k_{21}^{10}(T)$, the contribution of molecular attraction is much greater than single-quantum VV energy exchange; the ratios of the rate constants calculated
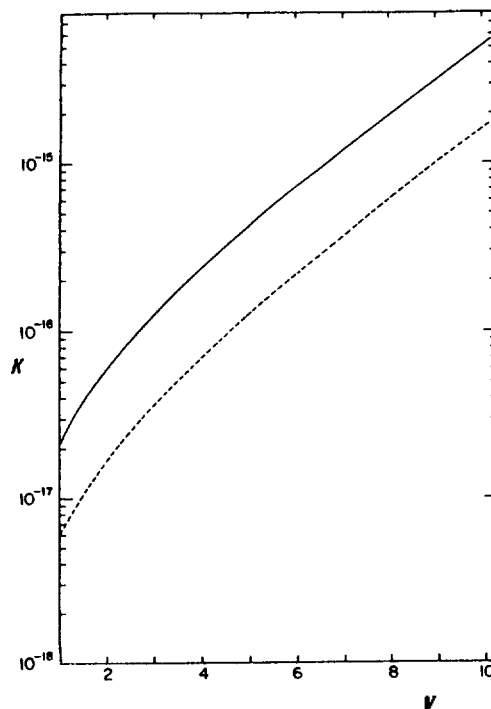
from the Morse potential to those from purely repulsive part of potential are 5.02 and 1.51 at 295 and 3000K, respectively. Moreover, at 100K the ratio is 20.7 which is over an order of magnitude increase in the predicted rate constant. The transition $2,0\rightarrow 0,2$ appears through $2,0\rightarrow 1,1\rightarrow 0,2$, that is, the single-quantum transitions twice. In order that the two-quantum transition appears, two molecules have to exist within the region of the collision for a sufficient time, that is, the time enough for at least two transitions. Thus, the effect of molecular attraction is very paramount for two-quantum exchange.

The dependence of VV energy exchange rate constants on v at 295K for the Morse-type interaction and the purely repulsive interaction, are shown in Figure 2. The ratios of the rate constant for the former to the latter are 3.49, 3.35 and 3.12 for v=2,5, and 10, respectively. This fact shows that the contribution of molecular attraction is nearly similar to all energy levels at 295K. At 3000K, the ratios are 1.36, 1.35, and 1.31 for v=2, 5, and 10, respectively; that is, at high temperature, the ratios are smaller than at low temperature but those are also similar for all energy levels. On the other hand, for the system involving the dipole-dipole interaction the effect of molecular attraction is very larger than the above N_2+O_2 system.[18,19] In particular for the system involving the strong attraction like the hydrogen bond, the different approach from the present model should be considered, for example, "long-lived collision".[4,7,8] But, for H_2+H_2 collision, for $1,1\rightarrow 2,0$ transition, the contribution of molecular attraction increases the rate constant of the purely repulsive interaction by a factor of 1.73 and 1.41 at 300 and 1000K, respectively. At 3000K, moreover, the molecular attraction increases k(T) of the repulsive interaction by a factor as small as 1.22 only.

Table 1. Energy Defects and the Ratios of the Rate Constant at 295K for the Morse Potential to the purely Repulsive Potential for Six Collision Pairs

System	Energy defect (cm⁻¹)	Ratio
$^{14}N_2(1) + O_2(0) \rightarrow {}^{14}N_2(0) + O_2(1)$	774	3.533
$^{15}N_2(1) + O_2(0) \rightarrow {}^{15}N_2(0) + O_2(1)$	696	3.354
$^{12}CO(1) + O_2(0) \rightarrow {}^{12}CO(0) + O_2(1)$	587	3.484
$^{13}CO(1) + O_2(0) \rightarrow {}^{13}CO(0) + O_2(1)$	540	3.244
$^{13}CO(1) + N_2(0) \rightarrow {}^{13}CO(0) + N_2(1)$	− 234	2.695
$^{12}CO(1) + N_2(0) \rightarrow {}^{12}CO(0) + N_2(1)$	− 187	2.603

Table 2. Rate constants for $HF(v) + HF(0) \rightarrow HF(v-1) + HF(1)$ at 300K

Process	Orientation average	$\theta_1 = 0°$[a] $\theta_2 = 65°$	Kwok-Wikins[b]
$2+0 \rightarrow 1+1$	113	8.5	9.9 ± 3.0
$3+0 \rightarrow 2+1$	21	9.8	15.7 ± 6.0
$4+0 \rightarrow 3+1$	7.2	10.	16.3 ± 6.0
$5+0 \rightarrow 4+1$	1.6	2.3	5.2 ± 3.0

[a]reference 4. [b]reference 23.

For $H_2 + H_2$ collision, D is only 33.3k, thus the ratios to be small. Therefore, for the system having the small molecular attraction, the use of the purely short-range interaction should be considerable.

On the other hand, in order to examine the contribution of molecular attraction for the energy mismatch, we have considered several systems. The systems, the energy defects, and the ratios of the rate constants for the Morse potential to those for the purely repulsive potential are presented in Table 1. In this table, it is shown that the extent of the contribution of a molecular attraction is decreased as the energy mismatch becomes smaller, but the extent is considerably small. This fact is explicit from the mentioned above, that is, $N_2(v) + O_2(0) \rightarrow N_2(v-1) + O_2(1)$, the energy mismatch is 745 cm⁻¹ for $v = 1$ and it decreases to 514 cm⁻¹ for $v = 10$.

The orientation dependence of the VV rate constant is shown in Figure 3. This quantity is obtained from Eq.(18) before making the average over θ_1 and θ_2. For $\theta_1 = \theta_2 = 0$ or π, i.e., the collinear configuration, the exchange is most efficient. The curve for the purely repulsive interaction shows that when the attractive force is neglected, the VV energy exchange rate is significantly lower than that using the Morse potential near the collinear configuration. The average of $k(T, \theta_1, \theta_2)$ over θ_1 and θ_2, i.e., eq(20) is 2.136×10^{-17} at 295K, which is close to the observed value of 8.0×10^{-18} [20] If we take $\theta_1 = 0$ and $\theta_2 = \pi$, the result is 7.5×10^{-17}, indicating that the model calcualtion which considers only a collinear configuration can significantly overestimate VV energy exchange rate, because such configuration would produce more efficient collision than the oriented ones. That is, the VV rate constant calculated for collinear configuration is greater than those for Eq.(20) because it excludes less efficient collision with other orientations. On the other hand, in the $HF(v) + HF(0) \rightarrow HF(v-1) + HF(1)$, there is a strong attractive force between two HF molecules owing to the hydrogen-bond interaction. The energetically preferred orientation for such attraction is the
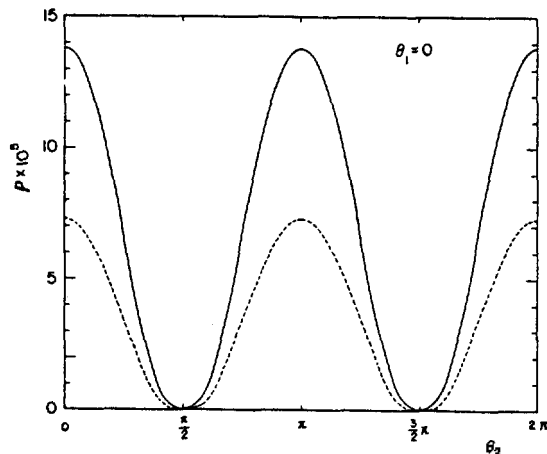

Figure 3. The orientation dependence of the VV rate constant for $N_2(1) + O_2(0) \rightarrow N_2(0) + O_2(1)$. The solid curve is calculated from Eq.(18) for the Morse potential and the broken curve is for the purely repulsive interaction.

interaction of the H atom of one molecule with F of the other. Thus, the molecules can neither make complete rotational motion nor rapid translational motion. The equilibrium separation r_e is 2.79Å, $\theta_{1e} = 0°$ and $\theta_{2e} = 60-70°$.[21,23] Shin *et al.*[4,24] have calculated the vibrational energy transfer probability on the base of the preferred orientation. They chose the equilibrium orientation angles to be $\theta_{1e} = 0°$, $\theta_{2e} = 65°$. To examine the orientation effect for this system, we calculated the energy exchange rate constants including the rotation average and the results are given in Table 2 with Shin's[4] and experimental data.[25] As shown in the table, the results calculated for the preferred orientation agree with the experimental data more than those for rotation average. This fact shows that the model of the preferred orientation must be considered for the system having strong attraction thus the preferred orientation.

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Calculation of the Dipole Moments for the Coordination Compounds with Organic Ligands such as $(C_2H_5)_2SO$, $(C_6H_5)_2SO$, $(C_6H_5)_2SeO$, $(C_6H_5)_3AsO$, $(C_6H_5)_3PBCl_3$, and $(C_2H_5)_2OZrCl_4$

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The dipole moments for some coordination compounds with organic ligands have been calculated adopting the molecuar orbitals obtained from EHT calculation with modified technique. Adopting the molecular orbitals with the modified technique, the calculated dipole moments for all the coordination compounds with organic ligands give closer agreements with experimental values than those using the molecular orbitals obtained from EHT calculation. The calculated dipole moments suggest that $(C_2H_5)_2SO$, $(C_6H_5)_2SO$, and $(C_6H_5)_2SeO$ may have a trigonal planar structure and $(C_6H_5)_3AsO$ and $(C_6H_5)_3PBCl_3$ a square planar structure and $(C_2H_5)_2OZrCl_4$ may be distorted markedly. This work may also indicate that the modified technique is superior to the EHT calculation as far as the dipole moment calculation is concerned.

Introduction

The vector additive method[1] was suggested by Thomson and he calculated the dipole moment of polyatomic molecules whose dipole moments can be considered as the resultant of the vectorial combination of the monents belonging to the individual bonds. For a molecule containing n bonds of different types, the dipole moment is given by[2]

$$\mu = \sum_{i=1}^{n} \mu_i \qquad (1)$$

where μ_i is the moment characterizing the i th bond. Evaluation of the dipole moments of polyatomic molecules were tried to obtain accurate dipole moments assuming component bond moments could be treated vectorially as represented by equation (1). However this approach, though roughly useful in many instances, failed to establish an exact additive principles because various intramolecular effects always operate in polyatomic molecules.

The quantum mechanical method of calculation for the dipole moments of polyatomic molecules has been developed after the vectorial scheme.[2] In this approach of calculation, the dipole moment for a given compound is defined by the relation[3]

$$\mu = -e \sum_i < \psi (1, 2, 3 \cdots) |r_i| \psi (1, 2, 3 \cdots) > + e \sum_j Z_j R_j \qquad (2)$$

where r_i is the radius vector of the i th electron and Z_j and R_j are the charge of the j th atomic nucleus and its radius vector, respectively. Such a quantum mechanical approach has enormous advantage over the vectorial additive method of calculation based on a set of empirically selected bond and group moments and enables all the effects not included in the framework of this scheme to be taken into account. However, the accuracy of dipole moments calculated by the quantum mechanical approach is also seriously limited by the degree of approximation of the function ψ to the true wave function of the molecule. Now, a fairly good approximation to the true wave functions for complex molecules can be obtained only by using empirical and semiempirical methods.[4]

It is impossible to calculate the dipole moments for coordination compounds with organic ligands such as $(C_2H_5)_2$ S O for example. Therefore first we adopt the model which is used to calculate the dipole moments for transition metal complexes,[5] and secondly the modified technique in calculating the dipole moments for square pyramidal complexes. Thus we may adopt the two assumptions[6] to apply the two approaches in dipole moments for coordination compounds with organic ligands in which the central metal atom in complexes may be replaced by the inorganic atom and all the inorganic ligands by organic ligands. Therefore, the coordination compounds with organic ligands may be considered to be organo metallic complexes in which only the central metal atoms are replaced by the inorganic atoms. We also assume that the trigonal planar symmetry is maintained for $(C_2H_5)_2SO$, $(C_6H_5)_2SO$ and $(C_6H_5)_2SeO$, the square planar symmetry for $(C_6H_5)_3AsO$ and $(C_6H_5)_3PBCl$ and the square pyramidal symmetry for $(C_2H_5)_2OZrCl_4$ even though two or three ligands in the coordination compounds are replaced by the organic