Proc. Natl. Acad. Sci. USA
Vol. 76, No. 8, pp. 3571–3575, August 1979
Chemistry

Effect of molecular rotation on the vibration–vibration energy transfer in condensed media

[donor (NH, ND)/acceptor (CO)/oscillators/guest molecules/host lattice]

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Contributed by Henry Eyring, February 21, 1979

ABSTRACT **The purpose of the present communication has been to present the derivation of the vibrational relaxation rate constant for the case in which both phonons and the molecular rotation (three-dimensional) participate in the vibrational relaxation and to study the effect of molecular rotation on the vibration–vibration energy transfer in the condensed phase. The experimental results of vibration–vibration energy transfer between donors, NH and ND, and acceptors, CO and ^{13}CO, have been analyzed.**

A theoretical model was presented for the vibrational energy transfer between the excited donor D and the unexcited acceptor A for the case in which both A and D are polar (1). It has been shown that the rate of vibrational energy transfer $K_{da}(T)$ is related to the rates of vibrational relaxation of D and A, $K_D(T)$ and $K_A(T)$, by

$$K_{da}(T) = \frac{|H'(2)_A|^2}{\hbar\omega_A^3} K_D(T)_{da} + \frac{|H'(2)_D|^2}{\hbar\omega_D^3} K_A(T)_{da}, \quad [1]$$

where $K_D(T)_{da}$ and $K_A(T)_{da}$ denote the vibrational relaxation rate constants of D and A with the energy gap $\omega_D - \omega_A$, the energy mismatch between D and A. $|H'(2)_A|^2$ and $|H'(2)_D|^2$ are defined by

$$|H'(2)_A|^2 = \frac{2|\vec{\mu}_D^0|^2|\vec{\mu}_A'|^2}{3\epsilon^2R^6};$$

$$|H'(2)_D|^2 = \frac{2|\vec{\mu}_D'|^2|\vec{\mu}_A^0|^2}{3\epsilon^2R^6}, \quad [2]$$

where

$$\vec{\mu}_D = \vec{\mu}_D^0 + \vec{\mu}_D'Q_D + \ldots; \quad \vec{\mu}_A = \vec{\mu}_A^0 + \vec{\mu}_A'Q_A + \ldots \quad [3]$$

In deriving Eq. 1, the second order time-dependent perturbation method has been used to describe the dipole interaction between D and A and the coupling of D and A with the heat bath so that the excess vibrational energy can be given up to the heat bath. In this communication, we shall apply the energy transfer rate expression $K_{da}(T)$ given by Eq. 1 to the experimental results of the energy transfer between donors NH and ND and acceptors CO and ^{13}CO in the rare gas matrices (2). It will be shown that in this case the rotational motion of NH or ND is important in accepting the energy mismatch between D and A in the vibrational energy transfer. The importance of molecular rotation in vibrational relaxation in condensed media has been pointed out by Brus and Bondybey (3), Legay (4), Freed *et al.* (5), and Berkowitz and Gerber (6).

GENERAL CONSIDERATION

From Eq. 1 we can see that $K_{da}(T)$ is related to the vibrational relaxation rate constants $K_D(T)_{da}$ and $K_A(T)_{da}$. If the vibrational relaxation is induced by a repulsive potential to describe the interaction between the molecular vibration and medium vibrations, then the vibrational relaxation rate constant, say for the donor D, $K_D(T)_{da}$ is given by

$$K_D(T)_{da} = \frac{C_D'^2}{\hbar(\omega_D - \omega_A)} \sqrt{\frac{\pi}{2\bar{\omega}(\omega_D - \omega_A)}} \times \exp\left[-\frac{(\omega_D - \omega_A)}{\bar{\omega}}\left\{\log\frac{(\omega_D - \omega_A)}{S_D\bar{\omega}} - 1\right\} + S_D\right], \quad [4]$$

where $\bar{\omega}$ represents the average frequency of phonons, S_D is the coupling constant, and C_D' represents the force acting on the molecular oscillator by the medium (1, 4, 7). In Eq. 4, $K_D(T)_{da}$ is expressed in the energy gap law form at $T = 0$. A general expression for $K_D(T)_{da}$ has been observed. It has been shown that at low temperatures the rate of vibrational relaxation is insensitive to temperature (4). Thus, for our purpose, the expression for the vibrational rate constant at $T = 0$ is sufficient.

As mentioned above, the molecular rotation has been shown in many cases to be important in accepting the vibrational excitation during vibrational relaxation. In treating the rotational effect, Freed *et al.* (5) have regarded the molecular rotation as a planar rotator and, for the interaction between the molecular vibration and rotation, they have used

$$\hat{H}' = X_D V_0 \exp(\alpha \cos n\phi), \quad [5]$$

where X_D represents the displacement of molecular vibration, ϕ is the rotation angle, and V_0, α, and n are constant. By using Eq. 5, the expression for the vibrational relaxation rate constant can easily be derived (5, 8). For example, in the free rotator approximation and at $T = 0$, we find

$$K_D(0)_{da} = \frac{V_0^2}{2\hbar\mu\omega_D(\omega_D - \omega_A)} \times \exp\left[-\frac{2}{n}\sqrt{\frac{\omega_D - \omega_A}{\omega_{rD}}}\left(\log\frac{2}{n\alpha}\sqrt{\frac{\omega_D - \omega_A}{\omega_{rD}}} - 1\right)\right], \quad [6]$$

where $\omega_{rD} = \hbar/2I_D$ and I_D is the moment of inertia of the donor D. Eq. 6 describes the experimental finding of the inverse deuterium effect and the energy dependence quite well.

THREE-DIMENSIONAL ROTATIONAL EFFECT

For simplicity we consider the system to consist of diatomics dissolved in monatomic crystals; the interaction between the host atom and guest atom is assumed to be of the Morse type (see Fig. 1).

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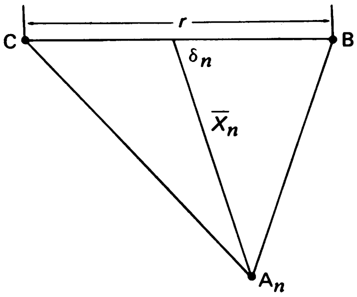

FIG. 1. Coordinate systems.

$$V = D_B\{1 - e^{-a_B(X_B - r_{Bo})}\}^2 + D_c\{1 - e^{-a_c(X_c - r_{co})}\}^2, \quad [7]$$

where

$$X_B^2 = \alpha^2 r^2 + \overline{X}^2 - 2\overline{X}\alpha r \cos\delta \quad [8]$$

and

$$X_c^2 = r^2(1-\alpha)^2 + \overline{X}^2 + 2\overline{X}r(1-\alpha)\cos\delta \quad [9]$$

with $\alpha = m_c/(m_B + m_c)$.

When $\overline{X} > r$, Eqs. **8** and **9** can be approximately expressed as

$$X_B = \overline{X}\left\{1 - \alpha\left(\frac{r}{\overline{X}}\right)\cos\delta + ..\right\} \quad [10]$$

and

$$X_c = \overline{X}\left\{1 + (1-\alpha)\left(\frac{r}{\overline{X}}\right)\cos\delta + ..\right\}(9). \quad [11]$$

If we let $r = r_0 + \Delta r$ where Δr represents the displacement of the diatomic molecule, then by expanding V in power series of Δr and collecting the linear terms we find the perturbation for vibrational relaxation as

$$\hat{H}' = \hat{H}'(R) + \hat{H}'(A), \quad [12]$$

where $\hat{H}'(R)$ denotes the contribution from the repulsive portion of V, and $\hat{H}'(A)$ represents the attractive contribution from V. They are given by

$$\hat{H}'(R) = 2\alpha\Delta r \sum_n \cos\delta_n \times \left\{a_B D_B e^{-2a_B(\overline{X}_n - r_{Bo})} e^{2a_B\alpha r_o\cos\delta_n} - a_c D_c \frac{(1-\alpha)}{\alpha} \times e^{-2a_c(\overline{X}_n - r_{co})} e^{-2a_c(1-\alpha)r_o\cos\delta_n}\right\} \quad [13]$$

and

$$\hat{H}'(A) = 2\alpha\Delta r \sum_n \cos\delta_n \times \left\{a_B D_B e^{-a_B(\overline{X}_n - r_{Bo})} e^{a_B\alpha r_o\cos\delta_n} + a_c D_c \frac{(1-\alpha)}{\alpha} \times e^{-a_c(\overline{X}_n - r_{co})} e^{-a_c(1-\alpha)r_o\cos\delta_n}\right\}. \quad [14]$$

Here the contribution from all over the host atoms has been taken into account by the summation over n.

Using $\hat{H}'$ given by Eq. **12**, the rate constant of vibrational relaxation can be calculated

$$k(T) = \frac{2\pi}{h}\sum_{\{v\}}\sum_{\{v'\}} P_{\{v\}}|\langle 1\{v\}|\hat{H}'|0\{v'\}\rangle|^2 \times \delta(\hbar\omega + E_{\{v\}} - E_{\{v'\}}) \quad [15]$$

for the transition 1 → 0 of the diatomics, where $\{v\}$, $\{v'\}$ are the quantum numbers of the accepting degrees of freedom and ω is the frequency of the molecular vibration. It is commonly believed that the repulsive portion $H'(R)$ is more important in vibrational relaxation than $\hat{H}'(A)$; so tentatively we shall ignore the contribution from $\hat{H}'(A)$. Using the relation (10)

$$e^{2a_B\alpha r_o\cos\delta_n} = \sum_{j=0}^{\infty}(2J+1)j_J(2\alpha a_B r_o)P_J(\cos\delta_n), \quad [16]$$

we find

$$\hat{H}'(R) = 2\alpha\Delta r\sum_n\sum_{J=0}^{\infty}F_J(\overline{X}_n)_n(2J+1)\cos\delta_n P_J(\cos\delta_n), \quad [17]$$

where $j_J(y)$ is the Bessel function and

$$F_J(\overline{X}_n)_n = a_B D_B e^{-2a_B(\overline{X}_n - r_{Bo})} j_J(2\alpha a_B r_o) - \frac{(1-\alpha)}{\alpha} a_c D_c e^{-2a_c(\overline{X}_n - r_{co})} \times (-1)^J j_J(2a_c(1-\alpha)r_o). \quad [18]$$

By expressing $P_J(\cos\delta_n)$ in terms of spherical harmonics $Y_{JM}(\theta_n\phi_n)$ and $Y_{JM}(\theta\phi)$, Eq. **17** becomes

$$\begin{aligned}\hat{H}'(R) &= 2\alpha\Delta r\sum_n\sum_J F_J(\overline{X}_n)_n\{(J+1)P_J + 1(\cos\delta_n) + JP_{J-1}(\cos\delta_n)\}\\ &= 8\pi\alpha\Delta r\sum_n\sum_{J=0}^{\infty}F_J(\overline{X}_n)_n \times \left\{\frac{J+1}{2J+3}\sum_{M=-J-1}^{J+1}Y_{J+1M}(\theta_n\phi_n)Y^*_{J+1M}(\theta\phi) + \frac{J}{2J-1}\sum_{M=-J+1}^{J-1}Y_{J-1M}(\theta_n\phi_n)Y^*_{J-1}(\theta\phi)\right\}. \quad [19]\end{aligned}$$

This expression is convenient for studying the participation of molecular rotation in vibrational relaxation. It should be noted that $F_J(\overline{X}_n)_n$ will provide the coupling between the molecular vibration and the translation of the guest molecule and the vibration of host atoms; in other words, $\hat{H}'(R)$ can provide us the information about the separate amount of the vibrational excitation going into molecular rotation and other degrees of freedom.

To be able to proceed with the derivation of $k(T)$, it is necessary to know the potential function for the molecular rotation. For simplicity, we shall assume that the rotation is free; for low barrier cases, this at least will provide us the zeroth order approximation. In this case, Eq. **15** can be written as

$$k_R(T) = \frac{2\pi}{\hbar}\sum_{JM\{v\}}\sum_{J'M'\{v'\}} \times P_{J\{v\}}|\langle 1JM\{v\}|\hat{H}'(R)|OJ'M'\{v'\}\rangle|^2 \times \delta(\hbar\omega + E_{J\{v\}} - E_{J'\{v'\}}), \quad [20]$$

where

$$\langle 1JM\{v\}|\hat{H}'(R)|OJ'M'\{v'\}\rangle = 8\Pi\alpha\langle 1|\Delta r|0\rangle\sum_n\sum_{J''=0}^{\infty}\langle\{v\} \times F_{J''}(\overline{X}_n)_n|\{v'\}\rangle\left\langle JM\left|\frac{J''+1}{2J''+3}\sum_{M''=-J''-1}^{J''+1} \times Y_{J''+1M''}(\theta_n\phi_n)Y^*_{J''+1M''}(\theta\phi) + \frac{J''}{2J''-1}\sum_{M''=-J''+1}^{J''} Y_{J''-1M''} \times (\theta_n\phi_n)Y^*_{J''-1M''}(\theta\phi)\right|J'M'\right\rangle. \quad [21]$$

Let us first consider the case $T = 0$. In this case, we are concerned with the calculation of

$$\langle 100\{v\}|\hat{H}'(R)|OJ'M'\{v'\}\rangle$$
$$= 2\alpha\sqrt{4\pi}\,\langle 1|\Delta r|0\rangle \sum_n \left\{\frac{J'}{2J'+1}\langle\{v\}|F_{J'-1}(\overline{X}_n)_n|\{v'\}\rangle + \frac{J'+1}{2J'+1}\langle\{v\}|F_{J'+1}(\overline{X}_n)_n|\{v'\}\rangle\right\} Y_{J'M'}(\theta_n\phi_n). \quad [22]$$

In Eq. **22**, the terms involved $F_{J'-1}$ and $F_{J'+1}$ will describe the energy of vibrational excitation relaxed into the molecular translation and host phonons. For comparison with the two-dimensional rotator model of Freed *et al.* (5), we shall consider the case in which $\overline{X}_n$s are not displaced; Eq. **22** then reduces to

$$\langle 100\{v\}|\hat{H}'(R)|OJ'M'\{v'\}\rangle = 2\alpha\sqrt{4\pi}\,\langle 1|\Delta r|0\rangle\, f_{J'\{v\}\{v'\}} I_{J'M'}, \quad [23]$$

where

$$f_{J'\{v\}\{v'\}} = \delta_{\{v\}\{v'\}}\left\{\frac{J'}{2J'+1}F_{J'-1}(\overline{X}) + \frac{J'+1}{2J'+1}F_{J'+1}(\overline{X})\right\} \quad [24]$$

and

$$I_{J'M'} = \sum_n Y_{J'M'}(\theta_n\phi_n). \quad [25]$$

Substituting Eq. **25** into Eq. **20** yields

$$k_R(0) = \frac{32\pi^2\alpha^2}{\hbar}|\langle 1|\Delta r|0\rangle|^2 f^2_{J'\{0\}\{0\}} \sum_{M'} |I_{J'M'}|^2 \rho(E_{J'}), \quad [26]$$

where $\hbar\omega = E_{J'}$ and the density of states $\rho(E_{J'})$ is given by

$$\rho(E_{J'}) \div \frac{(2J'+1)}{2}\sqrt{\frac{2I}{\hbar^2 E_{J'}}} \div \frac{2I}{\hbar^2} = \frac{1}{\hbar\omega_r}.$$

To find the analytical expression for $k_R(0)$ given by Eq. **26**, we use the approximate relation

$$j_J(z) = \frac{(2z)^J \cdot J!}{(2J+1)!}\left\{1 + \frac{\frac{z^2}{2}}{2J+3} + \frac{\left(\frac{z^2}{2}\right)^2}{2!(2j+3)(2J+5)} + \cdots\right\}. \quad [27]$$

It follows that

$$f_{J'\{o\}\{o\}} = a_B D_B e^{-2a_B(\overline{X}-r_{B_o})} \times \left\{\frac{J'}{2J'+1} j_{J'-1}(2\alpha a_B r_o) + \frac{J'+1}{2J'+1} j_{J'+1} \times (2\alpha a_B r_o)\right\} - \frac{(1-\alpha)}{\alpha} a_c D_c e^{-2a_c(\overline{X}-r_{co})}(-1)^{J'+1} \times \left\{\frac{J'}{2J'+1} j_{J'-1}(2a_c(1-\alpha)r_o) + \frac{J'+1}{2J'+1} \times j_{J'+1}(2a_c(1-\alpha)r_o)\right\} \quad [28]$$

or

$$f_{J'\{o\}\{o\}} \div \left\{a_B D_B e^{-2a_B(\overline{X}-r_{B_o})} - \frac{(1-\alpha)}{\alpha} a_c D_c e^{-2a_c(\overline{X}-r_{co})}(-1)^{J'+1}\right\} \times \left\{\frac{J'}{2J'+1} j_{J'-1}(2\alpha\bar{a}r_o) + \frac{J'+1}{2J'+1} j_{J'+1}(2\alpha\bar{a}r_o).\right. \quad [29]$$

In Eq. **29** an average quantity $\bar{a}$ has been introduced for a_B and a_c.

Using Eqs. **27** and **29**, we obtain

$$k_R(0) = \frac{32\pi\alpha^2}{\hbar^2\omega_r}|\langle 1|\Delta r|0\rangle|^2 G^2_{J'} \times \frac{(1+\bar{a}^2\alpha^2 r_o^2)^2}{(4\bar{a}\alpha r_o)^2}\left\{\frac{J'!\cdot(4\alpha\bar{a}r_o)^{J'}}{(2J'-1)!}\right\}^2, \quad [30]$$

where

$$G_{J'} = a_B D_B e^{-2a_B(\overline{X}-r_{B_o})} + \frac{(1-\alpha)}{\alpha} a_c D_c (-1)^{J'} e^{-2a_c(\overline{X}-r_{co})} \quad [31]$$

or

$$k_R(0) = \frac{16\pi\alpha^2}{\mu\hbar\omega\omega_r} G^2_{J'} \frac{(1+\bar{a}^2\alpha^2 r_o{}^2)^2}{(4\bar{a}\alpha r_o)}\left\{\frac{J'!\cdot(4\alpha\bar{a}r_o)^{J'}}{(2J'-1)!}\right\}^2, \quad [32]$$

where μ is the reduced mass of the diatomics. Eq. **32** can be put in the modified energy gap law form

$$k_R(0) = \frac{2\pi\alpha^2}{\mu\hbar\omega\omega_r} G^2_{J'} \frac{(1+\bar{a}^2\alpha^2 r_o{}^2)^2}{(\bar{a}\alpha r_o)^2} J'(J'+1) \times \exp\{-2J'\{\log J' - \log(\bar{a}e\alpha r_o)\}\}, \quad [33]$$

which should be compared with the result of the two-dimensional rotator model

$$k(0) = \frac{V_0{}^2}{2\mu\hbar\omega_{\mathrm{D}}(\omega_{\mathrm{D}} - \omega_{\mathrm{A}})} \times \exp\left\{-\frac{2}{n}\sqrt{\frac{\omega_{\mathrm{D}}-\omega_{\mathrm{A}}}{\omega_{r\mathrm{D}}}}\left(\log\frac{2}{n\alpha}\sqrt{\frac{\omega_{\mathrm{D}}-\omega_{\mathrm{A}}}{\omega_{r\mathrm{D}}}} - 1\right)\right\}. \quad [34]$$

APPLICATION

To show the application of the theoretical result to experimental data, in Table 1 we reproduce the experimental results for the energy transfer between NH and ND and ^{12}CO and ^{13}CO obtained by Goodman and Brus (2). For the first three sets of data in Table 1, they are able to fit them with the energy-gap law expression (see also Fig. 2):

$$K_{\mathrm{et}}\,(30\ \text{Å}) = 9.9 \times 10^4 \exp(-\Delta E/28\ \mathrm{cm}^{-1}), \quad [35]$$

where 30 Å represents the intermolecular distance between the excited donor and acceptor. From Eq. **1**, we can see that for the theoretical purpose it is required to have knowledge of $\vec{\mu}_{\mathrm{A}}{}^0$, $\vec{\mu}_{\mathrm{A}}{}'$, $\vec{\mu}_{\mathrm{D}}{}^0$, and $\vec{\mu}_{\mathrm{D}}{}'$. Both $\vec{\mu}_{\mathrm{A}}{}^0$ and $\vec{\mu}_{\mathrm{A}}{}'$ are known for CO (11) but only $\vec{\mu}_{\mathrm{D}}{}^0$ is known for NH ($A^3\pi$) (12). To estimate $\vec{\mu}_{\mathrm{D}}{}'$, Goodman and Brus (2) assumed that $\vec{\mu}_{\mathrm{D}}{}^0$ and $\vec{\mu}_{\mathrm{D}}{}'$ have the same relative

Table 1. Experimental results

Processes	ΔE, cm^{-1}	K_{et} (30 Å), sec^{-1}
ND ($v = 2$) → ^{13}CO	13	1.26×10^5
ND ($v = 1$) → ^{12}CO	78	6.50×10^3
ND ($v = 1$) → ^{13}CO	126	1.23×10^3
NH ($v = 1$) → ^{12}CO	729	5.2×10

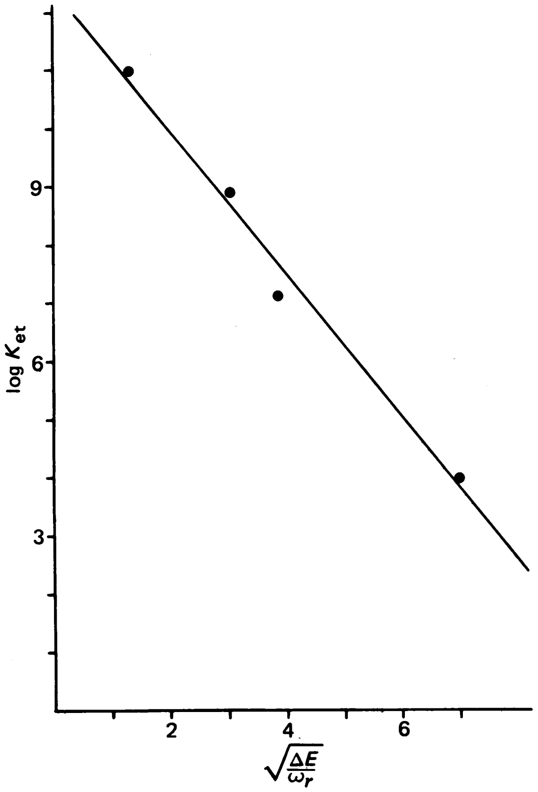

FIG. 2. Energy-gap law fitting of experimental results.

magnitude in NH ($A^3\pi$) as they do in HF, where both have been measured (13, 14), and obtained (2).

$$\vec{\mu}_D = 6.24 \times 10^{-18} + 3.2 \times 10^2\, Q \text{ ESU-cm}, \quad [36]$$

where Q has units of $\sqrt{g}$ cm. $\vec{\mu}_A{}^0$ and $\vec{\mu}_A{}'$ are given by (2, 11)

$$\vec{\mu}_A = 0.54 \times 10^{-18} + 4.42 \times 10^2\, Q \text{ ESU-cm}. \quad [37]$$

By using these values, Eq. 1 for the ND* case becomes (2)

$$K_{et}\,(30\ \text{Å}) = 3.05 \times 10^{-8} K_{ND}(\Delta E) + 1.03 \times 10^{-10}\, K_{CO}(\Delta E). \quad [38]$$

In view of the recent experimental results on the CO system (4, 15), the second term is negligible. By using this fact and the energy-gap law expression for $K_{ND}(\Delta E)$ (1, 7, 16), Eq. 35 can be deduced from Eq. 38. For the process NH($v = 1$) → ^{12}CO, correcting for the isotope effect yields $S \approx 0.1$ and $\bar{\omega} \approx 100$ cm^{-1} from which Eq. 35 gives K_{et} (30 Å) $\doteqdot 1.0 \times 10^{-7}$ sec^{-1} which should be compared with the experimental value of 5.2 × 10 sec. In other words, the use of $K_{ND}(\Delta E)$ or $K_{NH}(\Delta E)$ based on the multiphonon relaxation is incapable of interpreting the experimental results.

Next we consider the case in which we use the expression for $K_{ND}(\Delta E)$ or $K_{NH}(\Delta E)$ based on the rotational participation model. In this case, we expect that the plot of log $K_{et}(R)$ vs. $\sqrt{(\omega_D - \omega_A)/\omega_r}$ should be approximately linear. This is shown in Fig. 3. From Fig. 3 we can see that the linearity holds well for the four sets of the vibrational–vibrational energy transfer data. Notice that in Fig. 3 the last set of data in Table 1 is not corrected for the isotope effect; this can be done by subtracting the value in Fig. 3 by 0.347. That only brings the point above the line slightly down below the line. In other words, the linearity still holds well.

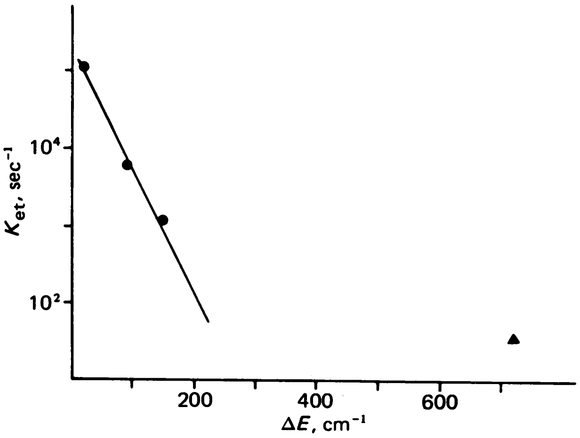

FIG. 3. Rotational effect on vibrational–vibrational energy transfer. ●, ND* → CO; ▲, NH* → CO.

For the quantitative purpose, we shall express Eq. 1 with the neglect of the second term in Eq. 1 as

$$\log K_{et}(R) = \log A - \log \frac{\Delta\omega}{\omega_r} - \frac{2}{n}\sqrt{\frac{\Delta\omega}{\omega_r}} \times \left(\frac{1}{2}\log\frac{\Delta\omega}{\omega_r} - \log\frac{n\alpha e}{2}\right), \quad [39]$$

where $\Delta\omega = \omega_D - \omega_A$ and $A = |H'(2)_A|^2/\hbar\omega_A{}^3 \cdot V_0{}^2/2\mu_D\hbar\omega_D\omega_r$. In analyzing the rotational effect on the vibrational relaxation, Freed *et al.* (5) find that for $n = 4$, $\alpha = 0.70$. By using these values and ω_r(HD) = 8.33 cm^{-1} from Legay's paper (4), we obtain log A = 10.79. From A, the V_o value can be determined.

As has been pointed out above, in our case of interest here, Eq. 1 takes the form,

$$K_{et}(R) = \frac{|H'(2)_A|^2}{\hbar\omega_A{}^3} K_D(\Delta E). \quad [40]$$

In other words, from $K_{et}(R)$ we can determine $K_D(\Delta E)$ and vice versa. Now we shall use Eq. 40 to predict the vibrational relaxation rate constant for donors ND and NH. For ND, we have ω_D = 2217 cm^{-1}, $\sqrt{\omega_D/\omega_r}$ = 16.30 and $K_{ND}(2217)$ = 1.6 × 10^4 sec^{-1}; the experimental result is $K_{ND}(2217) \leq 10^4$ sec^{-1}. Similarly, for NH we have ω_D = 2977 cm^{-1}, $\sqrt{\omega_D/\omega_r}$ = 14.28, and $K_D(2977)$ = 1.6 × 10^5, whereas the experimental result (17) is $K_D(2977)$ = 1.2 × 10^6 sec^{-1}. In the second case, there exists one order of magnitude discrepancy. In other words, for small energy-gap cases, the excess energy will almost completely relax into the rotation first, but for the large energy-gap case, a considerable amount of excess energy will simultaneously relax into the phonon bath. Furthermore, it should be noted in Eq. 40 that it has been assumed that the rotation is free. This may cause some error.

We thank the U.S. Research Office (Grant DAHC 04-75-0019) for financial support.

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