9. A representative propanation procedure is as follows: A solution of potassium iodide (7.0 g, 42 mmol) in 20 *ml* of water was added slowly to the solution of benzaldehyde (2.12 g, 20 mmol) and methyl bromocyanoacetate (7.12 g, 40 mmol) in 20 *ml* of ethanol at 25℃. After stirring for 10 hr at 25℃, the product was filtered and rinsed with 20 *ml* of cold ethanol. The obtained product was dried and recrystallized from 95% ethanol to give 2.6 g (45% yield) of $\mathbf{1}_b$.
10. Analytical data of $\mathbf{1}_{a-d}$ are as follows: $\mathbf{1}_a$: ^{1}H-NMR (acetone-d_6) δ 2.63 (s, 2H), 3.93 (s, 6H); IR (KBr) 3105, 3008 (propane ring C-H), 2240 (CN), 1745 (*trans* C=O), 1734 (*cis* C=O) cm^{-1}. Anal. Calcd for $C_9H_8N_2O_4$: C, 51.92; H, 3.85; N, 13.46. Found: C, 51.82; H, 3.83; N, 13.48. $\mathbf{1}_b$: ^{1}H-NMR (acetone-d_6) δ 3.86 (s, 6H), 3.93-4.10 (m, 1H), 7.30-7.71 (m, 5H); IR (KBr) 3023 (cyclopropane ring C–H), 2245 (CN), 1750 (*trans* C=O), 1737 (*cis* C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.23; N, 9.86. Found: C, 63.30; H, 4.28; N, 9.80. $\mathbf{1}_c$: ^{1}H-NMR (acetone-d_6) δ 3.87 (s, 6H), 4.23 (s, 1H), 7.67-7.99 (m, 4H); IR (KBr) 3075 (cyclopropane ring C–H), 2240, 2220 (CN), 1748 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.56; N, 13.59. Found: C, 62.08; H, 3.51; N, 13.51. $\mathbf{1}_d$: ^{1}H-NMR (acetone-d_6) δ 3.78-4.05 (m, 6H), 4.30 (s, 1H), 7.70-8.43 (m, 4H); IR (KBr) 3090, 3050 (cyclopropane ring C–H), 2250 (CN), 1758 (*trans* C=O), 1742 (*cis* C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{11}N_3O_6$: C, 54.71; H, 3.34; N, 12.77. Found: C, 54.63; H, 3.39; N, 12.70.

Vibrational Relaxation of Asymmetric Stretching Levels of Water Molecules in H_2O+Ar Collision

Jongbaik Ree* and Keun Ho Chung

Department of Chemistry Education,
College of Education Chonnam National University,
Kwangju 500-757

Hyung Kyu Shin

Department of Chemistry,
University of Nevada Reno, NV 89557, U.S.A.

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In the vibrational relaxation of H_2O molecules, following the excitation to the asymmetric stretching level (ν_3), relaxation can proceed through several different energy transfer pathways.[1-3] The equilibration of the ν_3 and ν_1 levels is very fast, being as fast as the gas kinetic collision rate.[2,4] The dominant path for the collisional deexcitation of these equilibrated stretching levels by a collision partner is relaxation down to the bending overtone ($2\nu_2$) level followed by relaxation of a single bending quantum to the bending fundamental (ν_2) level, which finally returns to the ground level. In recent paper, we reported the 001→020, 020→010, 010→000 transition probabilities in H_2O+Ar over the temperature range of 200-1000 K based on the vibration-to-rotation (VR) model,[5] where the energy release ΔE is removed by rotation. Calculated transition probabilities agree well with the recent experimental data[2] over the entire temperature range. Another path for the relaxation of stretching levels is down to the bending fundamental level, *i.e.*, 001→010 relaxation, which also finally returns to the ground level. The other path, *i.e.*, the direct relaxation to the ground level (001→000) involves a large energy mismatch ($\Delta E=3755$ cm^{-1}), and is expected to be much less efficient than the first two paths. The latter two paths are, of course, expected to be less efficient at low temperatures, but become more efficient at higher temperatures. Therefore, it is interesting to examine the relaxation rate for these different processes. For the latter two processes, the application of the model developed in Ref. 5 is so straightforward, that it is simple to study the effects of the relaxation. In this paper, we report such a study over the temperature range 200-1000 K and compare the results with those obtained for 001→020 relaxation rate.

In Ref. 5, we have shown the derivation of the VR energy transfer probability, for the 001→010 transition, the time evolution of oscillator state is

$$|\psi(t)>=\exp[g_1(t)a_2a_3^{+}]\exp[g_2(t)a_2^{+}a_3]\exp[g_3(t)a_2^{-}a_2] \times\exp[g_4(t)a_3^{+}a_3]\exp[g_5(t)\boldsymbol{I}]|001>, \tag{1}$$

where $\boldsymbol{I}$ is the identity operator and $g_i(t)$ is a complex valued function of time. Here a_i and a_i^{+} are ladder operators. The probability of 001→010 vibrational deexcitation is

$$P_{001\to010}=\lim_{t\to\infty}|g_2(t)\exp[g_4(t)+g_5(t)]|^2, \tag{2}$$

the following five differential equations have to be solved to calculate the transition probability,

$$i\hbar\dot{g}_1(t)=-g_1(t)\hbar(\omega_2-\omega_3)-g_1^2(t)F'_{11}(t)+F'_{11}(t) \tag{3a}$$

$$i\hbar\dot{g}_2(t)=g_2(t)\hbar(\omega_2-\omega_3)+2g_1(t)g_2(t)F'_{11}(t)+F'_{11}(t) \tag{3b}$$

$$i\hbar\dot{g}_3(t)=g_1(t)F'_{11}(t)+\hbar\omega_2 \tag{3c}$$

$$i\hbar\dot{g}_4(t)=-g_1(t)F'_{11}(t)+\hbar\omega_3 \tag{3d}$$

$$i\hbar\dot{g}_5(t)=\frac{1}{2}\hbar(\omega_2+\omega_3). \tag{3e}$$

Here $F'_{11}(t)=(\hbar/2\omega_2)^{\frac{1}{2}}(\hbar/2\omega_3)^{\frac{1}{2}}F_{11}(R,\ \theta)$, which is the interaction potential responsible for 001→010 transition and defined in Ref. 5. The function $g_5(t)$ *is simply* $\exp[-i(\omega_2+\omega_3)t]$ and others are obtained numerically.

For the 001→000 transition, the quantum state needed in determining the transition probability is

$$|\psi(t)>=\exp[g_1(t)a_3^{+}]\exp[g_2(t)a_3]\exp[g_3(t)a_3^{+}a_3] \times\exp[g_4(t)\boldsymbol{I}]|001>, \tag{4}$$

where $\boldsymbol{I}$ is also the identity operator. The transition probability is

$$P_{001\to000}=\lim_{t\to\infty}|g_2(t)\exp[g_3(t)+g_4(t)]|^2, \tag{5}$$

where g_i's are the solutions of

$$i\hbar\dot{g}_1(t)=\hbar\omega_3g_1(t)-F'_{01}(t) \tag{6a}$$

$$i\hbar\dot{g}_2(t)=-\hbar\omega_3g_2(t)+F'_{01}(t) \tag{6b}$$

Table 1. Calculated Transition Probabilities for H_2O+Ar at Various Temperatures

T(K)	$P_{001\to020}$[a]	$P_{001\to010}$	$P_{001\to000}$
200	1.686 (−3)[b]	8.425 (−5)	6.431 (−6)
300	2.240 (−3)	1.270 (−4)	9.959 (−6)
500	3.203 (−3)	2.298 (−4)	1.905 (−5)
700	3.882 (−3)	3.695 (−4)	3.153 (−5)
1000	5.511 (−3)	6.636 (−4)	5.969 (−5)

[a] This means the probability for H_2O (001)+Ar→H_2O (020)+Ar.
[b] 1.686 (−3)=1.688×10^{-3}.

$$i\hbar\dot{g}_3(t)=\hbar\omega_3 \tag{6c}$$

$$i\hbar\dot{g}_4(t)=g_1(t)F'_{01}(t)+\frac{1}{2}\hbar\omega_3, \tag{6d}$$

where $F'_{01}(t)=(\hbar/2\omega_3)^{\frac{1}{2}}F_{01}(R,\ \theta)$, which is responsible for 001→000 transition.

Potential constants used in the calculation are the same as in Ref. 5. The thermal averaged transition probability can be written in the form[5]

$$\begin{aligned}P_{i\to f}(T)=(1/2\pi)\int_0^{2\pi}d\theta_0\int_0^{R^*}(2b/R^{*2})db\int_0^{\infty}E/(kT)^2\\ \exp(-E/kT)dE\times\int_0^{\infty}(1/E_R\pi kT)^{\frac{1}{2}}\\ \exp(-E_R/kT)dE_R\,P_{i\to f}(E_R,\ E,\ b,\ \theta_0).\end{aligned} \tag{7}$$

In the present VR model, where the energy release ΔE is removed by rotation, we replace the rotational energy E_R in the probability expression by the symmetrized energy $E_R=1/4[(E_R+\Delta E)^{\frac{1}{2}}+E_R^{\frac{1}{2}}]^2$, which is equivalent to taking the average velocity $\Omega=(\Omega_i+\Omega_f)/2$.

In Table 1, we present calculated values of both $P_{001\to010}$ and $P_{001\to000}$ from 200 to 1000 K and compare them with $P_{001\to020}$. The probability $P_{001\to020}$ increases from 1.686×10^{-3} at 200 K to 5.511×10^{-3} at 1000 K. These values are in agreement with experimental data over the entire temperature range.[2] As shown in the table, the probabilities $P_{001\to010}$ are much smaller than the former. The probability at 200 K is 5% compared to $P_{001\to020}$, increasing up to 12% as the temperature increases up to 1000 K. It is interesting to note that these effects become more efficient at higher temperature. The direct relaxation probabilities from the asymmetric stretching level to the ground level are considerably inefficient compared to the deexcitation to the former two processes. The probabilities $P_{001\to000}$ are markedly smaller, being only ~0.5% compared to $P_{001\to020}$ at 200 K and ~1% at 1000 K, respectively. Comparing the above results, we first note that the major source of these differences of probabilities is the energy mismatch ΔE. For the transition 001→020, the amount of energy released is only 604 cm^{-1}, whereas the energy mismatch ΔE is 2160 cm^{-1} for the transition 001→010 and as great as 3755 cm^{-1} for the 001→000 energy transfer process. Thus the 001→020 transition process appears to be of major importance in the relaxation of the asymmetric stretching level. On the other hand, the transition 001→020 involves three vibrational levels in the relaxation; *i.e.*, $v_3=1\to0$ and $v_2=0\to1\to2$. For the transition 001→010, two vibrational levels are involved; *i.e.*, $v_3=1\to0$ and $v_2=0\to1$. However, the 001→000 energy transfer process involves only one vibrational level; $v_3=1\to0$. We expect that the three-quantum process is less efficient than the two-quantum process, and two-quantum process is less efficient than the single quantum process, if the energy mismatches are all the same.[5] In the above processes, however, the single quantum process involves much greater energy mismatch than the multiquantum processes, so the energy transfer probabilities are remarkably small. But it is noteworthy that two-quantum process (001→010) becomes efficient as the temperature increases despite the larger energy mismatch. On the other hand, because of the vibration-to-translation (VT) probability become more efficient relative to the VR probability at higher temperatures, we shall discuss the VT mechanism here. When we invoke the VT model, ΔE is then removed by translation, so E in Eq. (7) have to be replaced by $E=1/4\{[E(1-b^2/R^{*2})+\Delta E]^{\frac{1}{4}}+[E(1-b^2/R^{*2})]^{\frac{1}{4}}\}^2$. The calculated VT probabilities for $P_{001\to010}$ and $P_{001\to000}$ are 3.295×10^{-4} and 1.213×10^{-5}, respectively. These values are at most ~50% and ~25% of the VR values, and also much smaller than $P_{001\to020}$. These VT values at 300 K are about two orders of magnitude smaller than those of VR. Therefore, we conclude that the relaxation of H_2O (001) by Ar can be interpleted by the deexcitation to the bending overtone level over the temperature range of 200-1000 K.

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References

1. R. T. Tung and R. E. Center, *J. Chem. Phys.*, **62**, 2187 (1975).
2. P. F. Zittle and D. E. Masturzo, *J. Chem. Phys.*, **90**, 977 (1989).
3. J. Finzi, F. E. Hovis, V. N. Panfilov, P. Hess, and C. B. Moore, *J. Chem. Phys.*, **67**, 4053 (1977).
4. J. Ree and H. K. Shin, *Chem. Phys. Lett.*, **163**, 308 (1989).
5. J. Ree and H. K. Shin, *J. Chem. Phys.*, **93**, 6463 (1990).