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Production Yields of H(D) Atoms in the Reactions of $N_2(a'\,^1\Sigma_u^-)$ with H_2O, D_2O, and HOD

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The deactivation processes of $N_2(a'\,^1\Sigma_u^-, v = 0)$, the lowest metastable singlet-state molecular nitrogen, by H_2O, D_2O, and HOD were investigated. The overall rate constants as well as the quantum yields for the production of H(D) atoms were determined. $N_2(a', v = 0)$ was produced by energy transfer from $N_2(a\,^1\Pi_g, v = 0)$, while $N_2(a, v = 0)$ was produced by a two-photon excitation of the ground-state N_2. The rate constants for the deactivation by H_2O and D_2O were determined to be $(4.22 \pm 0.27) \times 10^{-10}$ and $(4.21 \pm 0.11) \times 10^{-10}$ $cm^3\,s^{-1}$, respectively, by measuring the decay profiles of $N_2(a, v = 0)$ under equilibrated conditions. The quantum yields for the production of H(D) atoms were determined to be $0.9\,^{+0.1}_{-0.2}$ both for H_2O and D_2O under the assumption that the only exit for $H_2(D_2)$ is the production of two H(D) atoms. In a reaction with HOD, the yield ratio of [H]/[D] was measured to be 1.0 ± 0.1. This lack of the isotope effect suggests that the decomposition proceeds by forming bound intermediate complexes, such as HNNOD and DNNOH.

Recently, we have studied the reactions of the lowest metastable singlet-state molecular nitrogen, $N_2(a'\,^1\Sigma_u^-, v = 0)$, with H_2, CH_4, and their deuterated species.[1] It was revealed that the rate constants are large and that the major exit channels involve chemical bond scission. Since the lowest metastable triplet-state nitrogen, $N_2(A\,^3\Sigma_u^+)$, is rather unreactive against H_2 and CH_4, as well as H_2O,[2] $N_2(a'\,^1\Sigma_u^-)$ can be one of the initiators in a series of reactions in active nitrogen.

The elimination of H(D) atoms is one of the major exit channels in the reaction of $N_2(a', v = 0)$ with $CH_4(CD_4)$. The production yields were determined to be 0.7 both for CH_4 and CD_4. In addition, the yield ratio of [H]/[D] was found to be unity in the reaction with CH_2D_2. This lack of the preferential production of H or D atoms is noteworthy because large kinetic isotope effects have been widely recognized in many systems. For example, in the photodissociation of partially deuterated hydrocarbons, the C–H bond scission is preferred compared to the C–D bond scission by a factor of two or more.[3–9] A similar preferential production of H atoms over D atoms has also been observed in the reactions of $O(^1D_2)$ and $N(^2D)$ with partially deuterated methanes.[10–12] The lack of an isotope effect in the reaction with CH_2D_2 is consistent with a mechanism which assumes the formation of $HNNCH_3$-type intermediate complexes during the deactivation process.[1] In this model, the production yields of H and D atoms depend only on the rate constants for the formation of the $DNNCH_2D$ and $HNNCHD_2$ complexes. Only a minor isotope effect is expected in such complex formation processes. If the lifetime of the complexes is short, only H atoms are expected to be produced from $HNNCHD_2$, while only D atoms from $DNNCH_2D$. Although the lifetime of the complexes may change by isotope substitution, the production yields may depend little on the lifetime if the major fate of the complexes is the elimination of H or D atoms. This complex-formation model is consistent with the electronic structure of CH_4. The vertical excitation energy of CH_4 is higher than the electronic energy of $N_2(a', v = 0)$ and direct energy transfer cannot be efficient.[13]

The situation is different in the quenching of $N_2(a', v = 0)$ by H_2O. The vertical excitation energy to produce the excited singlet-state $H_2O(\tilde{A}\,^1B_1)$ is lower than the electronic energy of $N_2(a', v = 0)$.[14] In other words, O–H bond dissociation after direct energy transfer is energetically possible. The two dissociation processes, direct energy transfer and complex formation mechanisms, can be distinguished by examining the H/D isotope effect in HOD. In the direct photolysis of HOD at 157 nm, the preferential production of H atoms has been observed.[15,16] Shafer et al. have reported that the [H]/[D] ratio is 4, while Yang et al. have proposed that it is 2.5. In the photodissociation at 193 nm, the ratio is as large as 12.[17] If HOD decomposes unimolecularly after energy transfer, a similar large H/D isotope effect should be observed. On the other hand, no such isotope effect is expected if the reaction proceeds via intermediate complexes.

In the present study, the reactive processes of $N_2(a', v = 0)$ with H_2O, D_2O, and HOD were examined. The yields for the production of H(D) atoms were determined, besides the overall reaction rate constants, to elucidate the quenching mechanism.

Experimental

The experimental apparatus and the procedure were similar to those described elsewhere.[1] A frequency-doubled output of a Nd:YAG laser pumped dye laser (Quanta-Ray, GCR-170/PDL-3) at 289.9 nm was focused with a 200 mm focal-length lens to two-photon excite ground-state N_2 to the $a\,^1\Pi_g$, $v = 0$ level. Base-shifted Rhodamine 610 was used as a laser dye. The pulse energy of the laser was around 10 mJ. $N_2(a, v = 0)$ may easily be relaxed by collisions with N_2 to produce $N_2(a', v = 0)$.[1,18–20] The production of triplet-state N_2 is spin-forbidden, while relaxation to the ground state is too exothermic. $N_2(a, v = 0)$ and $N_2(a', v = 0)$ may easily be equilibrated. In general, the decay rate of equilibrated states represents the weighted average of those of the two components. In the present system, however, the population is shifted to $N_2(a', v = 0)$; the population ratio of $N_2(a, v = 0)$ to $N_2(a', v = 0)$ is 1/184. Under such conditions, the decay profile represents the removal process of $N_2(a', v = 0)$, and it is possible to evaluate the rate constant for the quenching of $N_2(a', v = 0)$ by analyzing the decay profiles of $N_2(a, v = 0)$.[1] The $N_2(a, v = 0)$ density was measured by laser-induced fluorescence using another Nd:YAG laser-pumped dye laser (Quanta-Ray, GCR-170 and Lambda Physik, LPD3000E). The excitation wavelength was 250.0 nm, while the vacuum-ultraviolet fluorescence around 120 nm was monitored.[1] The typical probe pulse energy was 0.5 mJ. The quencher pressures were kept much lower than that of N_2 in order to make sure of the equilibration between $N_2(a)$ and $N_2(a')$.

H(D) atoms produced in the reactions of $N_2(a', v = 0)$ with H_2O(D_2O or HOD) were detected by a two-photon laser-induced fluorescence technique at 243.2 nm.[1,12] The vacuum ultraviolet fluorescence (Lyman α) was collimated with an MgF_2 lens and detected with a solar-blind photomultiplier tube through an interference filter. In order to determine the H(D)-atom production yield for H_2O(D_2O), the D(H)-atom signal from D_2(H_2) was used as a standard. The typical pump-probe delay was 1.0 µs. The N_2 pressure was kept much higher than those of H_2O(D_2O) and D_2(H_2). In order to reduce the diffusional loss of H and D atoms, He was added to the system. The typical probe pulse energy was 0.4 mJ. The inside of the vacuum apparatus was passivated well, typically for one week, with the reactant gas, H_2O, D_2O or their mixture, before measurements. All of the measurements were carried out at 293 ± 3 K.

N_2 (Teisan, 99.999%), H_2 (Takachiho, 99.99995%), D_2 (Sumitomo Seika, isotopic purity 99.5%), and He (Teisan, 99.995%) were used from cylinders without further purification. Distilled and deionized H_2O was used after being degassed under a vacuum. D_2O was the product of Aldrich (isotopic purity 99.9%).

Results

The overall rate constants for the quenching of $N_2(a', v = 0)$ can be determined by analyzing the decay profiles of $N_2(a, v = 0)$ under equilibrated conditions at various quencher pressures.[1] Figure 1 shows a linear relationship between the reciprocal time constant for the decay and the H_2O pressure. The N_2 pressure was kept at 10.7 kPa. A similar plot was obtained for D_2O. From the slopes of such plots, the overall rate constants can be determined. The results are summarized in Table 1, together with the results for $N_2(A, v = 0)$. The error limits are the standard errors.

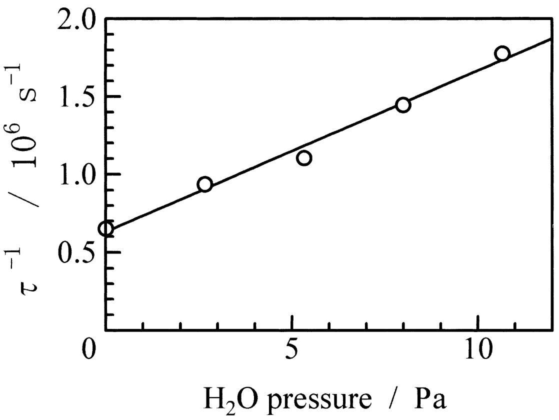

Fig. 1. Reciprocal time constant for the decay of equilibrated $N_2(a, v = 0)$ and $N_2(a', v = 0)$, τ^{-1}, as a function of H_2O pressure. The N_2 pressure was 10.7 kPa.

Table 1. Rate Constants for the Quenching of $N_2(a'\ ^1\Sigma_u^-, v = 0)$ and $N_2(A\ ^3\Sigma_u^+, v = 0)$ in Units of 10^{-11} cm^3 s^{-1}

Reactant	$N_2(a'\ ^1\Sigma_u^-, v = 0)$	$N_2(A\ ^3\Sigma_u^+, v = 0)$
N_2	0.020 ± 0.001 [a)]	$< 3 \times 10^{-7}$ [c)]
H_2	2.8 ± 0.1 [a)]	3.5×10^{-4} [c)]
D_2	1.7 ± 0.1 [a)]	$< 2 \times 10^{-3}$ [d)]
CH_4	28.8 ± 2.1 [a)]	3×10^{-4} [c)]
CH_2D_2	23.9 ± 2.5 [a)]	
CD_4	25.6 ± 2.3 [a)]	
H_2O	42.2 ± 2.7 [b)]	5×10^{-3} [c)]
D_2O	42.1 ± 1.1 [b)]	1.1×10^{-2} [d)]

a) Umemoto et al.[1] b) This work. c) Herron.[2] d) Golde et al.[25]

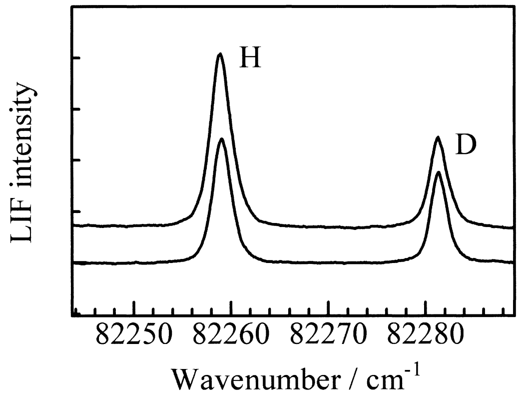

Fig. 2. Two-photon laser-induced fluorescence spectra of H and D atoms measured in the $N_2/H_2O/D_2/He$(upper) and $N_2/H_2/D_2/He$(lower) systems. The pump-probe delay was 1.0 μs. The partial pressures of H_2O and H_2 were 27 Pa. The pressures of D_2, N_2, and He were 133 Pa, 26.7 kPa, and 50.7 kPa, respectively, in the $H_2O/D_2/N_2/He$ system, while those were 27 Pa, 10.7 kPa, and 66.7 kPa in the $H_2/D_2/N_2/He$ system. The vertical scales were adjusted to give the same integrated intensities for the D-atom signals.

The absolute yield for the production of H atoms in the reaction of $N_2(a', v = 0)$ with H_2O was determined by comparing the laser-induced fluorescence signal intensities of H over D for two mixtures, $H_2O/D_2/N_2/He$ and $H_2/D_2/N_2/He$. Figure 2 shows the two-photon laser-induced fluorescence spectra in these systems. D_2 was added to normalize the signal intensities and make it possible to compare the H-atom signal intensities for H_2O and H_2. The pressures of H_2O and H_2 were 27 Pa in both systems. The pressures of D_2, N_2, and He were 133 Pa, 26.7 kPa, and 50.7 kPa, respectively, in the $H_2O/D_2/N_2/He$ system, while those were 27 Pa, 10.7 kPa, and 66.7 kPa in the $H_2/D_2/N_2/He$ system. The vertical scales of Fig. 2 were adjusted to give the same integrated intensities for the D-atom signals in the two systems. The ratio of the relative signal intensities is given by the H-atom production yields, $\phi(H_2)$ and $\phi(H_2O)$, and the rate constants for the overall quenching, k_{H_2} and k_{H_2O}:

$$\frac{([H]/[D])_{H_2O}}{([H]/[D])_{H_2}} = \frac{27}{133}\,\frac{k_{H_2O}}{k_{H_2}}\,\frac{\phi(H_2O)}{\phi(H_2)}.$$

By integrating the spectral lines shown in Fig. 2, the ratio of the signal intensity for H_2 to that for D_2 was determined to be 1.6 ± 0.2, while the ratio of the signal intensity for H_2O to that for D_2 was determined to be 2.2 ± 0.1. The error limits are standard errors. These ratios were independent of the pump-probe delay time between 0.5 and 2.0 μs, the pump laser energy between 6 and 10 mJ, and the probe laser energy between 0.3 and 0.6 mJ. Consistent results were obtained when the H_2O and H_2 pressures were changed by a factor of two. The rate constant for H_2 (k_{H_2}) was determined to be $(2.8 \pm 0.1) \times 10^{-11}$ cm^3 s^{-1} in our previous work,[1] while that for H_2O (k_{H_2O}) was measured to be $(4.22 \pm 0.27) \times 10^{-10}$ cm^3 s^{-1} in the present work. It may be assumed that dissociation to two H atoms, $N_2(a', v = 0) + H_2 \rightarrow N_2 + 2H$, is the sole exit channel for H_2, i.e. $\phi(H_2) = 2$.[1] Then, the yields for the production of H atoms in the reaction of $N_2(a', v = 0)$ with H_2O is determined to be $0.9^{+0.1}_{-0.2}$. Here, since the production of two H atoms, $N_2(a', v = 0) + H_2O \rightarrow N_2 + O + H + H$, is 110 kJ mol^{-1} endothermic, a quantum yield larger than unity was excluded. A similar result was also obtained in the quenching of $Xe(^3P_{0,2})$, whose energy is almost the same as that of $N_2(a', v = 0)$.[21] The production of $O(^1D_2) + H_2$ or $O(^3P) + H_2$ is minor in both systems. The yield for the production of D atoms in the $N_2(a', v = 0)/D_2O$ system was determined similarly to be $0.9^{+0.1}_{-0.2}$.

The ratio of the H-atom yield to the D-atom yield in the reaction of $N_2(a', v = 0)$ with HOD was determined by using a 1:1 mixture of H_2O and D_2O. HOD should be produced by just mixing H_2O and D_2O in the liquid phase. A typical two-photon LIF spectrum for this system is shown in Fig. 3. The H-atom signal intensity is just a little more intense than that of the D-atom signal; the [H]/[D] ratio is 1.07 ± 0.05. The population ratio of $[H_2O]:[HOD]:[D_2O]$ in the gas phase may not be the same as that in the liquid phase because of the difference in the vapor pressures. Plusquellic et al. calculated the $[H_2O]:[HOD]:[D_2O]$ ratio in the gas phase at 298 K to be 1.00:1.81:0.89.[17] This ratio was confirmed by our mass-spectrometric analysis using a quadrupole mass-spectrometer (Anelva, M-QA200TS). Since the rate constants for the overall quenching of $N_2(a', v = 0)$ as well as the quantum yields for the production of H(D) are the same for H_2O and D_2O, it is reasonable to assume that those for HOD are the same. By subtracting the H- and D-atom signals attributable to H_2O and D_2O, the ratio of the yield for H atoms to that for D atoms produced from HOD is calculated to be 1.0 ± 0.1. It should be noted that no H-atom signal was observed in the N_2/D_2O system, while no D-atom signal was observed in the N_2/H_2O system after passivation.

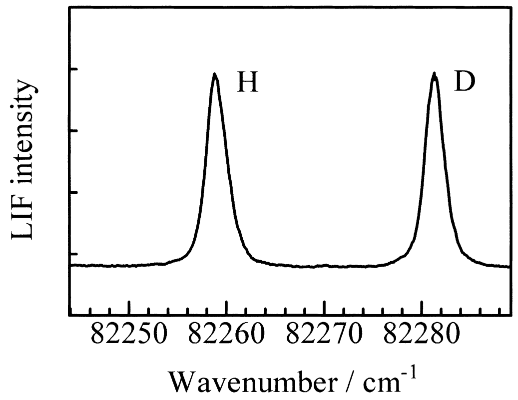

Fig. 3. Two-photon laser-induced fluorescence spectrum of H and D atoms measured in the $N_2/H_2O/HOD/D_2O/He$ system. The pump-probe delay was 1.0 μs. The partial pressures of H_2O, HOD, and D_2O were 14, 26, and 13 Pa, while those of N_2 and He were 26.7 and 50.7 kPa, respectively.

Discussion

The rate constants for the overall quenching of $N_2(a', v = 0)$ are much larger than those for $N_2(A, v = 0)$, not only for CH_4 and H_2, but also for H_2O, as are shown in Table 1, although the electronic configurations of $N_2(a')$ and $N_2(A)$ are the same. The slow rate constant for the quenching of $N_2(A, v = 0)$ by H_2 has been explained by the presence of an activation barrier.[22] Similar explanation may be possible for CH_4. In both cases, direct energy transfer is energetically inaccessible, and intermediate complexes must be formed for chemical quenching.[13,23] The electronic energy of the lowest triplet-state H_2O, $^3B_1$, is almost the same as that of $N_2(A, v = 0)$.[24] However, the production of this state in the energy transfer from $N_2(A, v = 0)$ requires a non-vertical deactivation of N_2 and the energy transfer efficiency may be small. In the collisional deactivation of vibrationally excited $N_2(A)$, the efficiency is much larger.[25]

In the quenching of $N_2(a', v = 0)$ by H_2O, vertical energy transfer is energetically possible. The electronic energy of $N_2(a', v = 0)$ is higher than that of the lowest singlet excited-state of H_2O, $\tilde{A}\ ^1B_1$.[26] Then, one of the possible explanations for the efficient production of H atoms should be the decomposition of electronically excited H_2O produced by direct energy transfer. $H_2O(\tilde{A}\ ^1B_1)$ correlates to $OH(X\ ^2\Pi) + H$ under the C_s symmetry.[14,27] Another possible mechanism is chemical quenching via intermediate complexes, which has been shown to be important in the quenching of H_2 and CH_4. In the latter mechanism, the singly occupied π_g^*2p orbital of $N_2(a')$ donates an electron to the empty σ^* orbital on the O–H bonds, while the filled σ orbital of O–H back donates to the $\pi_u 2p$ orbital, in a localized bond orbital picture. The two mechanisms, direct energy transfer and complex formation, can be distinguished by examining the H/D isotope effect in HOD.

The lack of an isotope effect in the quenching of $N_2(a', v = 0)$ by HOD strongly suggests that the latter mechanism is more probable. In general, a large isotope effect is expected in bond scission processes, such as abstraction. Minor effects are expected in insertion or addition reactions. In the direct photodissociation of HOD, O–H bond scission is preferred compared to the O–D bond scission by a factor of two or more.[15–17] An isotope effect by this factor is expected in a direct energy-transfer mechanism. A similar large isotope effect is expected if abstractive processes, such as $N_2(a', v = 0) + HOD \rightarrow N_2H$

+ OD → N_2 + H + OD, play some roles. The lack of an isotope effect suggests that HNNOH-type intermediate complexes must be formed during the deactivation process. In this model, the production yields of H and D atoms depend only on the rate constants for the formation of HNNOD and DNNOH. This is because only H atoms are expected to be produced from HNNOD and only D atoms from DNNOH. The production yields may depend little on the lifetime of the complexes if the production of H(D) atoms is the only exit.

The small Franck-Condon factor for the (0,0) band of the N_2(a′–X) transition cannot explain the lack of a direct energy-transfer process. The Franck-Condon factor for the N_2(a′–X) transition is largest at the (0,4) band.[28] The available energy for this transition is 700 kJ mol^{-1}. This energy is still enough to excite the ground-state H_2O to the $\tilde{A}\ ^1B_1$ state vertically. The presence of electronic states, which can be excited vertically, is not a sufficient condition for direct energy transfer. This may be true for the quenching of N_2(A) by inefficient quenchers, such as H_2O and CF_3Cl, in which cases a correlation has been observed between the rate constant and the photoabsorption cross section.[25]

Conclusions

$N_2(a'\ ^1\Sigma_u^-, v = 0)$ is quenched efficiently by H_2O and D_2O. The rate constants are as large as 4.2×10^{-10} $\mathrm{cm}^3\ \mathrm{s}^{-1}$ which are three or four orders of magnitude larger than those for $N_2(A\ ^3\Sigma_u^+, v = 0)$. The quantum yields for the production of H(D) atoms are near unity. Since $N_2(a'\ ^1\Sigma_u^-, v = 0)$ is the lowest metastable singlet-state molecular nitrogen, this state should be one of the strongest candidates for the initiators of chemical reactions in active nitrogen. No preferential production of H or D atoms was observed in the reaction with HOD. This lack of an isotope effect suggests that the O–H(O–D) bond scission cannot be characterized by decomposition after energy transfer. HNNOD and DNNOH ring-type intermediate complexes must be formed during the deactivation process.

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