# Production yields of H(D) atoms in the reactions of N[2](A [3]Σu[+]) with C[2]H[2],C[2]H[4], and their deuterated variants

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# Production yields of H(D) atoms in the reactions of $N_2(A\ ^3\Sigma_u^+)$ with $C_2H_2$, $C_2H_4$, and their deuterated variants

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The production yields of H(D) atoms in the reactions of $N_2(A\ ^3\Sigma_u^+)$ with $C_2H_2$, $C_2H_4$, and their deuterated variants were determined. $N_2(A\ ^3\Sigma_u^+)$ was produced by excitation transfer between Xe(6s $[3/2]_1$) and ground-state $N_2$ followed by collisional relaxation. Xe(6s $[3/2]_1$) was produced by two-photon laser excitation of Xe(6p $[1/2]_0$) followed by concomitant amplified spontaneous emission. H(D) atoms were detected by using vacuum-ultraviolet laser-induced fluorescence (LIF). The H(D)-atom yields were evaluated from the LIF intensities and the overall rate constants for the quenching which were determined from the temporal profiles of the NO tracer emission. The absolute yields were evaluated by assuming that the yield for $NH_3(ND_3)$ is 0.9. Although no H/D isotope effects were observed in the overall rate constants, there were isotope effects in the H(D)-atom yields. The H-atom yields for $C_2H_2$ and $C_2H_4$ were 0.52 and 0.30, respectively, while the D-atom yields for $C_2D_2$ and $C_2D_4$ were 0.33 and 0.13, respectively. The presence of isotope effects in yields suggests that $H_2(D_2)$ molecular elimination processes are competing and that molecular elimination is more dominant in deuterated species than in hydrides.

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## I. INTRODUCTION

The lowest triplet-state molecular nitrogen, $N_2(A\ ^3\Sigma_u^+)$, is one of the most important species in active nitrogen and plays important roles in plasma chemistry.[1,2] Since the electronic energy of $N_2(A)$, 601 kJ $mol^{-1}$, is large enough to break many chemical bonds, it has been proposed that radical species are produced in the reactions of $N_2(A)$ with unsaturated hydrocarbons.[3,4] However, no quantitative data are available, although Meyer *et al.* have reported that the H-atom yield in the quenching of $N_2(A)$ by $C_2H_4$ is rather low, from their final product analysis results.[5] The overall rate constants for the deactivation of $N_2(A)$ have been reported by many investigators.[1] It has been shown that the rate constants are large for unsaturated hydrocarbons, but small for saturated hydrocarbons and some closed-shell inorganic molecules, such as $H_2$ and $N_2$. This is in contrast to the lowest excited singlet-state molecular nitrogen, $N_2(a'\ ^1\Sigma_u^-)$. Efficient production of H atoms has been confirmed in the reactions of $N_2(a')$ with $H_2$, $CH_4$, and $H_2O$.[6-8]

$N_2(A\ ^3\Sigma_u^+)$ is often produced by the energy transfer from $Ar(4s\ ^3P_{0,2})$ to $N_2$ in discharge-flow systems.[1,5,9-12] In this technique, the production of atomic nitrogen is minor and this procedure has been regarded as a clean source of $N_2(A)$. However, the electronic energy of $Ar(4s\ ^3P_{0,2})$ is higher than those of some metastable triplet-states of molecular nitrogen, such as $B'\ ^3\Sigma_u^-$ and $W\ ^3\Delta_u$,[13] and the production of these species may not be ignored. In some cases, metastable Xe atoms, such as $Xe(6s\ [3/2]_2)$ and $Xe(6s'\ [1/2]_0)$, are used instead of $Ar(4s\ ^3P_{0,2})$.[14-17] The energy levels of $Xe(6s\ [3/2]_2)$ and $Xe(6s'\ [1/2]_0)$ are lower than the dissociation limit of $N_2$, but still higher than those of $N_2(B')$ and $N_2(W)$. When these excited rare gas atoms are produced in glow discharges, the total pressure must be low, in the order of 100 Pa. Under such conditions, highly excited metastable molecular nitrogen, such as $N_2$(B') and $N_2$(W), may not be deactivated completely. The incomplete quenching of these highly excited species may lead to a large error in yield measurements when the quantum yield for the reaction of $N_2$(A) is small. Fraser and Piper have tried to determine the O-atom yield in the reaction of $N_2$(A) with $O_2$ by using a discharge-flow apparatus and found that the apparent yield is 6.6.[12] This unreasonably high yield suggests the contribution of excited species other than $N_2$(A) under their low-pressure conditions.

$N_2$(A) can be produced under high-pressure conditions by the energy transfer from laser-excited Xe atoms. Recently, the present author has succeeded in the production of equilibrated $N_2$(B $^3\Pi_g$) and $N_2$(W $^3\Delta_u$) by the energy transfer from Xe(6s $[3/2]_1$).[18] Xe(6s $[3/2]_1$) was produced by two-photon laser excitation of Xe(6p $[1/2]_0$) followed by concomitant amplified spontaneous emission. This technique was originated by Alekseev and Setser.[19,20] $N_2$(A) can also be produced just by increasing the $N_2$ pressure. The present author has already confirmed the production of $N_2$(A) in this system by observing the emission from NO(A $^2\Sigma^+$) produced by energy transfer.[18] The rate constant for the quenching of Xe(6s $[3/2]_1$) and that of equilibrated $N_2$(B) and $N_2$(W) by $N_2$ have been determined to be $1.4 \times 10^{-11}$ and $2.9 \times 10^{-12}$ $cm^3s^{-1}$, respectively.[18] In the presence of 13.3 kPa of $N_2$, Xe(6s $[3/2]_1$) is quenched within 0.02 μs, while $N_2$(B) and $N_2$(W) are removed within 0.1 μs, and excited species other than $N_2$(A) may be removed in the presence of a sufficient amount of $N_2$ within a short time. It should be remembered that the quenching of $N_2$(A) by $N_2$ itself is extremely inefficient.[1] In the present work, this energy transfer technique from Xe(6s $[3/2]_1$) was employed to determine the quantum yields for the production of H(D) atoms in the quenching of $N_2$(A) by unsaturated hydrocarbons and their deuterated variants.

## II. EXPERIMENT

The experimental apparatus and the procedure were similar to those described elsewhere.[18,21] The frequency-doubled output of a dye laser (Lambda Physik, LPD3000E or Quanta-Ray, PDL-3) pumped with a Q-switched Nd:YAG laser (Quanta-Ray, GCR-170 or PRO-190) at 249.6 nm was used to two-photon excite ground-state Xe to the 6p $[1/2]_0$ level. Xe(6s $[3/2]_1$) can be produced selectively from Xe(6p $[1/2]_0$) through amplified spontaneous emission (ASE) at 828.0 nm. The typical pulse energy was 1 mJ and it was not necessary to focus the laser beam to cause the two-photon excitation and ASE.

The production of $N_2(A\ ^3\Sigma_u^+)$ was confirmed by observing the tracer emission of NO around 236 nm, the (0,1) band of the $A\ ^2\Sigma^+$ - $X\ ^2\Pi$ system. This $\gamma$-system emission was monitored at an angle perpendicular to the laser beam with a photomultiplier tube (Hamamatsu Photonics, R212UH) through a monochromator (JASCO, CT25C). The photomultiplier signal was processed with a digital oscilloscope (LeCroy, 6051A). From the quencher pressure dependence of the decay profiles, it is possible to evaluate the rate constants for the quenching. Detection of $N_2(A)$ by a cavity ringdown technique around 619 nm, the (4,0) band of the $B\ ^3\Pi_g$ - $A\ ^3\Sigma_u^+$ system, was also tried, but this was obscured by the thermal lens effect by the pump laser pulse.

In the detection of H(D) atoms, a second dye laser pumped with a Nd:YAG laser (Quanta-Ray, GCR-170/PDL-3) was used. Ground-state H(D) atoms were excited to 2p $^2P_J$ states by vacuum-ultraviolet (vuv) laser pulses at 121.6 (121.5) nm, Lyman-$\alpha$. The typical delay time between the pump and probe laser pulses was 10 μs. The procedures to produce Lyman-$\alpha$ radiation were similar to those described elsewhere.[21,22] The output of the dye laser around 729.6 nm was doubled in frequency by a $KH_2PO_4$ crystal and then tripled by a mixture of Kr and Ar. An autotracker (Inrad, Autotracker III) was used to adjust the angle of the crystal when the wavelength was scanned. The typical pressures of Kr and Ar were 13 and 40 kPa, respectively, while the laser pulse energy at the doubled stage was 3 mJ. The doubled output around 364.8 nm was focused into the tripling cell, 15 cm in length, by a 120 mm focal-length lens. The resulting vuv light was collimated with a 100-mm focal length $MgF_2$ lens (Oken) and entered the reaction vessel made of stainless steel. The induced fluorescence was detected at an angle perpendicular to the laser beam with a solar-blind photomultiplier tube (Hamamatsu Photonics, R6835) through an $MgF_2$ collimating lens and an interference filter (Acton Research, 122-N). The inside of the photomultiplier housing was flushed with dry nitrogen flow. The photomultiplier signal was processed with a gated boxcar averager (Stanford Research Systems, SR240/SR250/SR280) and a computer. The two-photon laser-induced fluorescence techniques, both at 243 nm to excite to H(2s $^2S$) and at 205 nm to excite to H(3s $^2S$, 3d $^2D$) employed in previous studies,[22,23] cannot be used in the presence of $NH_3$ because of efficient two-photon decomposition.

Measurements of the photoabsorption coefficients at Lyman-α were necessary, in some cases, to correct the LIF signal intensities. For this purpose, a small vessel filled with 130 Pa of NO was attached to the end of the reaction vessel to determine the transmittance of the vuv radiation.[21,22] The $NO^+$ ions produced by the vuv laser radiation were collected by parallel electrodes and the ion current was measured with the gated boxcar averager. All the measurements were carried out at 293 ± 3 K.

$N_2$ (Teisan or Japan Air Gases, 99.999%), $NH_3$ (Takachiho, 99.999%), NO (Nihon Sanso, 99%), $C_2H_4$ (Sumitomo Seika, 99.9%), He (Japan Air Gases, 99.999%), Ar (Nihon Sanso or Japan Air Gases, 99.999%), Kr (Nihon Sanso, 99.995%), and Xe (Teisan, 99.995%) were used from cylinders without further purification. $C_2D_4$ was obtained from ICON Stable Isotopes (isotopic purity 99%). $ND_3$ (Aldrich, isotopic purity 99%)

was separated from its $D_2O$ solution. $C_2H_2(C_2D_2)$ was synthesized from $CaC_2$ (Katayama Kagaku) and $H_2O(D_2O)$. $D_2O$ was obtained from Aldrich (isotopic purity 99.9%). $ND_3$, $C_2H_2$, and $C_2D_2$ were purified by repeated trap-to-trap distillations by using appropriate slush baths. In order to avoid H/D exchange, the vacuum system was exposed to $D_2O$ vapor for more than one week before the introduction of $ND_3$.

## III. RESULTS

### A. Overall rate constants for the quenching of $N_2(A)$

The overall rate constants for the quenching of $N_2(A)$ can be determined by measuring the quencher pressure dependence of the decay profiles of the NO tracer emission. The emission decayed exponentially after a short rise, and the decay rate increased linearly with the increase in the quencher pressure. Figure 1 shows the reciprocal time constants for the decay of the NO(A-X) emission in $Xe/N_2/NO/C_2H_2$ and $Xe/N_2/NO/C_2H_4$ systems as a function of $C_2H_2$ or $C_2H_4$ pressure. The pressures of Xe, $N_2$, and NO, measured with capacitance manometers, were 267 Pa, 2.67 kPa, and 1.3 Pa, respectively, while the quencher pressures were changed between 0.0 and 3.2 Pa. Under such conditions, the time constant for the decay was on the order of 10 μs. This slow decay must correspond to the quenching processes of $N_2(A)$ because the production of Xe(6s $[3/2]_1$) as well as $N_2(A)$ must be much faster. The radiative decay of NO(A) is also fast.[13] The slopes of the plots shown in Fig. 1 correspond to the overall rate constants for the quenching of $N_2(A)$. Similar results were obtained for other quenchers and the results are summarized in Table I, together with the results reported by other investigators. The agreement is fair, except for that of $NH_3$ reported by Callear and Wood.[26]

### B. Quantum yields for the production H(D) atoms

The absolute quantum yields for the production of H atoms in the quenching of $N_2(A)$ by unsaturated hydrocarbons can be determined by comparing the laser-induced fluorescence intensities of H atoms, since the absolute H-atom yield for $NH_3$ has been reported to be near unity.[10,11] The problem is that unsaturated hydrocarbons as well as $NH_3$ absorb the vuv radiation around Lyman-α to reduce the LIF signal intensity. In order to avoid this problem, the H/D signal ratio in the $Xe/NH_3/C_2D_2/N_2$ and Xe/unsaturated hydrocarbon/$C_2D_2/N_2$ systems were measured. In this case, the D-atom signal from $C_2D_2$ can be used as a standard. Figure 2 shows the typical LIF spectra. The partial pressures of Xe, $NH_3$, $C_2D_2$, $C_2H_2$, $C_2H_4$, and $N_2$ were 667 Pa, 1.3 Pa, 1.3 Pa, 1.3 Pa, 1.3 Pa, and 13.3 kPa, respectively. There were no systematic changes in the H/D signal ratios when the $N_2$ pressure was changed between 6.67 and 26.7 kPa, 13.3 kPa of He was added, the $C_2D_2$ and $C_2H_2$ pressures were doubled, or when the pump-probe delay time was increased from 10 to 20 μs. These ratios did not show any systematic changes when the laser intensities were reduced to half the signal intensities, either. No H(D)-atom signals were observed in the absence of the pump laser showing that the photodissociation by the probe laser is unimportant. As for $C_2H_2$ and $C_2H_4$, corrections are necessary for the difference in the absorption coefficients at the absorption peaks by H and D atoms, but the correction factors are small. This point will be discussed later. The overall reaction scheme can be represented as follows:

$$Xe^* \rightarrow Xe + h\nu \qquad (k_1),$$

$$Xe^* + N_2 \rightarrow Xe + N_2^* \qquad (k_2),$$

$$N_2^* + RH \rightarrow N_2 + R + H \qquad (\alpha k_3),$$

$$N_2^* + RH \rightarrow \text{other products} \qquad ((1-\alpha)k_3),$$

$$N_2^* + C_2D_2 \rightarrow N_2 + C_2D + D \qquad (\beta k_4),$$

$$N_2^* + C_2D_2 \rightarrow \text{other products} \qquad ((1-\beta)k_4),$$

$H+h\nu' \rightarrow H^*$ ($I_H$),

$H^* \rightarrow H+h\nu'$ ($k_r$),

$H^*+N_2 \rightarrow H+N_2$ ($k_5$),

$D+h\nu'' \rightarrow D^*$ ($I_D$),

$D^* \rightarrow D+h\nu''$ ($k_r$),

$D^*+N_2 \rightarrow D+N_2$ ($k_6$).

Here, Xe* stands for Xe(6s $[3/2]_1$) and $N_2$* represents $N_2$(A $^3\Sigma_u^+$). H* and D* represent H(2p $^2P_J$) and D(2p $^2P_J$), respectively. RH stands for $C_2H_2$, $C_2H_4$, or $NH_3$. The rate constants are represented by $k_i$, while the intensities of the vuv laser pulses are given by $I_H$ and $I_D$. It is assumed that the production of Xe* is instantaneous and that the quenching processes of Xe(6p $[1/2]_0$) by RH and $C_2D_2$ are minor. The natural radiative lifetime of Xe(6p $[1/2]_0$) is 26.8 ns.[36] Under the conditions that ASE takes place, the effective lifetime must be much shorter than this. The pressures of RH and $C_2D_2$ are too low to contribute to quenching. The quenching by $N_2$ may not be completely ignored, but if some highly excited states of $N_2$ are produced, they must be relaxed rapidly by collisions with $N_2$. The direct quenching of Xe* by RH and $C_2D_2$ must also be minor since the $N_2$ pressure is four orders of magnitude higher. The rate constants for the quenching of Xe* by $C_2H_2$, $C_2D_2$, and $C_2H_4$ are larger than that by $N_2$, but the difference is just two orders of magnitude.[18,21] The rate constant for the quenching of Xe* by $NH_3$ was measured in the present study to be $(7.33 \pm 0.22) \times 10^{-10}$ $cm^3s^{-1}$, which is a little less than that for $C_2H_4$, $(7.99 \pm 0.19) \times 10^{-10}$ $cm^3s^{-1}$.[18] It is also assumed that $N_2$(A) is produced directly from Xe* and $N_2$. This is not strictly true since the author has already shown that $N_2$(B) is one of the main products.[18] However, in the presence of an excess amount of $N_2$, it is possible to assume that the collisional relaxation of the precursor states, like $N_2$(B), is fast and that quenching of the precursor states by RH and $C_2D_2$ is minor.

For example, in the presence of 13.3 kPa of $N_2$, the pseudo-first-order rate constant for the decay of $N_2(B, v=0)$ is $9.6 \times 10^6$ $s^{-1}$, while that by 1.3 Pa of $C_2H_4$ is just $6.1 \times 10^4$ $s^{-1}$. The quenching of H*(D*) by RH and $C_2D_2$ are not taken into account for the same reason. Finally, the energy pooling between two $N_2$* molecules and the production of highly excited species can be ignored under the present conditions. The transmittance of the 249.6-nm radiation was measured by using a long absorption vessel, 100 cm in length. When the Xe pressure was 1.33 kPa, the transmittance was 91%. No absorption was observed when the wavelength of the laser was off-resonant or when $N_2$ was introduced instead of Xe. The pulse energy was 1 mJ, which corresponds to $1 \times 10^{15}$ photons/pulse. The beam radius was 3 mm. This corresponds to the excited Xe-atom density of $2 \times 10^{12}$ $cm^{-3}$. Under the present experimental conditions, at 667 Pa, that should be $1 \times 10^{12}$ $cm^{-3}$. This is the maximum density of $N_2$*. The rate constant for the energy pooling between two $N_2$* molecules is $3 \times 10^{-10}$ $cm^3s^{-1}$.[17] Then, the time constant for the decay of $N_2$* by energy pooling must be longer than 3 ms, which is much longer than the present time scale.

When the above reaction scheme is assumed, the H(D)-atom densities should be given by:

$$[\mathrm{H}] = \frac{\alpha k_3[\mathrm{RH}]}{k_3[\mathrm{RH}] + k_4[\mathrm{C_2D_2}]}[\mathrm{N_2}^*]_0\left[1 - \exp\{-(k_3[\mathrm{RH}] + k_4[\mathrm{C_2D_2}])t\}\right],$$

$$[\mathrm{D}] = \frac{\beta k_4[\mathrm{C_2D_2}]}{k_3[\mathrm{RH}] + k_4[\mathrm{C_2D_2}]}[\mathrm{N_2}^*]_0\left[1 - \exp\{-(k_3[\mathrm{RH}] + k_4[\mathrm{C_2D_2}])t\}\right]$$

Here, $[N_2^*]_0$ is the density of $N_2$* just after the production. The ratio of the LIF signal for H, $S_H$, to that for D, $S_D$, should be time independent and given by:

$$\frac{S_H}{S_D} = \frac{I_H \alpha k_3[\mathrm{RH}](k_r + k_6[\mathrm{N_2}])}{I_D \beta k_4[\mathrm{C_2D_2}](k_r + k_5[\mathrm{N_2}])},$$

since the LIF signal intensity should be proportional to the product of the probe laser intensity, the H(D)-atom density, and the yield of fluorescence. From the relative LIF intensity measurements, it is possible to determine the relative values of $\alpha k_3$. The values of $k_3$ were determined from the temporal profile measurements of the $N_2^*$ density in the present work. Since the absolute yield for the production of H atoms from $NH_3$ has been reported to be 0.9,[10,11] it is possible to scale the relative values of $\alpha$ into the absolute ones. The results are summarized in Table II.

Similar measurements were carried out to determine the D-atom yields for unsaturated deuterated carbons, such as $C_2D_4$. In this case, $ND_3$ was used as a standard and the H/D signal ratios were measured in $Xe/ND_3/C_2H_2/N_2$ and Xe/unsaturated deuterated carbon/$C_2H_2/N_2$ systems. The results are also summarized in Table II. Although no H-atom signals were observed in the $Xe/C_2D_2/N_2$ and $Xe/C_2D_4/N_2$ systems, small signals of H atoms were observed in the $Xe/ND_3/N_2$ system. This contribution was routinely corrected in the data analysis.

Corrections for the difference in the absorption coefficients at Lyman-$\alpha$ for H atoms and those for D atoms are necessary for $C_2H_2$ and $C_2H_4$.[21] The difference in the absorption coefficients was determined by measuring the transmitted vuv laser intensity. The absorption coefficients at Lyman-$\alpha$(H) and Lyman-$\alpha$(D) by $C_2H_2$ were determined to be 2010 and 1600 $atm^{-1}cm^{-1}$, respectively (1 atm = 101.3 kPa). The path length of the LIF detection was 14 cm, while the $C_2H_2$ pressure was 1.3 Pa. Then, the correction factor should be 1.07. The absorption coefficients at Lyman-$\alpha$(H) and Lyman-$\alpha$(D) by $C_2H_4$ were determined to be 810 and 750 $atm^{-1}cm^{-1}$, respectively. The correction factor is 1.01 at 1.3 Pa. No corrections are necessary for other quenchers. For example, the absorption coefficients by $C_2D_2$ are much smaller than those by $C_2H_2$; 90 and 110 $atm^{-1}cm^{-1}$, respectively, at Lyman-$\alpha$(H) and Lyman-$\alpha$(D).

In order to confirm that the precursor of H(D) atoms in the present systems is $N_2(A)$, not Xe(6s $[3/2]_1$) or $N_2(B)$, the growth curves of the H(D)-atom densities were recorded. Figure 3 shows the result in the Xe/$C_2D_2$/$N_2$ system. The solid line represents the experimental result, while the dashed line represents the calculated profile based on the rate constant listed in Table I, under the assumption that the only precursor of D atoms is $N_2(A)$. A similar result was obtained in the Xe/$C_2H_2$/$N_2$ system. The agreement between the experimental and calculated results suggests not only that the precursor of H(D) atoms is $N_2(A)$ but also that the diffusional loss of H(D) atoms is minor under the present conditions.

## IV. DISCUSSION

Meyer *et al.* have reported that the only condensable final product in the reaction of $N_2(A)$ with $C_2H_4$ is $C_2H_2$.[5] They have suggested that the molecular elimination, $N_2(A) + C_2H_4 \rightarrow N_2 + C_2H_2 + H_2$, is the only major process. Their conclusion is not in quantitative agreement with the present result that the H-atom yield is 0.30±0.05. The production of radical species in the pulsed radiolysis of a mixture of $N_2$ and $C_2H_4$ has been confirmed by Umemoto *et al.*[37] Under their conditions, the $N_2$ pressure was as high as 93 kPa and excited species other than $N_2(A)$, such as N($2p^3\ {}^2D$) and $N_2(a'\ {}^1\Sigma_u^-)$, must have been quenched rapidly by $N_2$.[6,38] Similar radical production was also confirmed for $C_2H_2$.[37] The importance of molecular elimination processes for $C_2H_4$ will be discussed later.

There is no doubt that π electrons of ethyne and ethene play important roles in the quenching of $N_2(A)$ since the rate constant for the quenching by ethane is extremely small.[1] If $N_2(A)$ can abstract H atoms from $C_2H_2$ or $C_2H_4$, similar processes may take place for $C_2H_6$. The lack of the H/D isotope effect in the quenching rate constants supports the energy transfer mechanism to produce triplet-state species. The triplet-state molecules thus produced must decompose to eject H(D) atoms. These situations are different from the quenching processes of $N_2(a'\ ^1\Sigma_u^-)$ and $N(2p^3\ ^2D)$ by methane. In the former $N_2(a')$ system, intermediate complexes are formed and H(D) atoms are ejected from the complexes.[6] In the latter system, $N(2p^3\ ^2D)$ inserts into the C-H(C-D) bonds to eject H(D) atoms. The production of NH(ND) has also been confirmed.[23]

In order to make clear the energetics, density functional calculations were carried out. The computational procedure was similar to that described elsewhere.[39] A Gaussian03 program was used and the geometry optimization was carried out at the B3LYP/6-31G(d) level while the potential energies and the zero point energies were evaluated at the B3LYP/6-31+G(d,p) level of theory.[40] The differences between the optimized energies of the vibrational ground states of the lowest singlet states and those of the lowest triplet states were calculated as follows:

| | |
|---|---|
| $N_2$ | 668.7 kJ $mol^{-1}$, |
| $NH_3$ ($ND_3$) | 500.9 (511.4) kJ $mol^{-1}$, |
| $C_2H_2$ ($C_2D_2$) | 344.8 (344.9) kJ $mol^{-1}$, |
| $C_2H_4$ ($C_2D_4$) | 251.3 (253.9) kJ $mol^{-1}$. |

Values in parentheses are those for deuterated species. The present calculated result for $N_2$ is not in quantitative agreement with the experimental value. The calculated value is 12% higher than the experimental one, 595.2 kJ $mol^{-1}$.[13] However, the above values may be used for semi-quantitative discussion, and they clearly show that the formation of triplet states is possible for all quenchers examined. This is true when the following vertical excitation energies are considered:

| | |
|---|---|
| $NH_3$ | 617.6 kJ $mol^{-1}$, |
| $C_2H_2$ | 531.9 kJ $mol^{-1}$, |

$C_2H_4$ 411.7 kJ mol$^{-1}$.

In the case of $NH_3$, the electronic energy of the triplet state is larger than the bond dissociation energy of H-$NH_2$, 434.5 kJ mol$^{-1}$, and this should be the only major exit channel, although the production of NH(X $^3\Sigma^-$) and $H_2$ is also exothermic. Mänz *et al.* have demonstrated that the lowest triplet state of $NH_3$, $\tilde{a}$ $^3A''_2$, correlates to NH(X)+$H_2$ and this channel is energetically more favorable than the $NH_2$+H channel,[41] but this may not be the case judging from the experimentally obtained high yields of H atoms.[10,11]

The H/D isotope effects observed in yields cannot be explained by the difference in state densities. As for $C_2H_2$ and $C_2H_4$, the electronic energies of the triplet states are less than those of the C-H bond scission energies. It is possible to explain the H-atom yields less than unity by considering that triplet states below the dissociation limits are produced. However, it is difficult to explain the large H/D isotope effect in yields by this model. The C-H(C-D) bond dissociation energy of $C_2H_2$($C_2D_2$) is calculated to be 550.3(557.8) kJ mol$^{-1}$. If the available energy is partitioned into all the degrees of freedom statistically, including the translational and internal energies of $C_2H_2$ and $N_2$, the probability to produce triplet-state $C_2H_2$ with its internal energy over the C-H bond dissociation energy is 0.61. That for $C_2D_2$ is calculated to be 0.58. The procedures of statistical calculations are similar to those described elsewhere.[42,43] The vibrational frequencies of triplet-state $C_2H_2$($C_2D_2$) were evaluated by density functional calculations. Although there are at least three triplet states for $C_2H_2$, $^3B_2$, $^3A_u$, and $^3B_u$, below the electronic energy of $N_2$(A),[44-46] only the lowest one, $\tilde{a}$ $^3B_2$, was considered for simplicity. The calculated quantum yield for $C_2H_2$ is in fair agreement with the experimentally obtained one, 0.52, but that for $C_2D_2$ is too large. Although the state density of $C_2D_2$ is much higher than that for $C_2H_2$, the relative state-density distributions are similar. The minor isotope effect appearing in this statistical model, 0.61 *vs.* 0.58, is mainly caused by the difference in available energies. It is also impossible to explain the results for $C_2H_4$ and $C_2D_4$ by the statistical model. The C-H(C-D) bond dissociation energy for $C_2H_4$($C_2D_4$) was calculated to be 451.1(461.1) kJ mol$^{-1}$. According to the above statistical model, the H(D)-atom yield for $C_2H_4$($C_2D_4$) is expected to be over 0.9, much larger than the experimental one. It is also hard to explain the quantum yields less than unity by collisional stabilization. If this is the case, the yields must depend on the total pressure. As has been mentioned, the yields depended little on the $N_2$ pressure between 6.67 and 26.7 kPa. In addition, there was no change when 13.3 kPa of He was added. The present results should represent the low-pressure limits. The present results cannot be explained by the efficient tunneling of H atoms, either. The H(D)-atom ejection process is an inverse of a radical recombination process and no potential barrier, except a centrifugal one, is expected. In addition, the lifetimes of the triplet states may be affected by tunneling but the yields may not if the atom ejection process is the only channel.

The presence of the H/D isotope effects in yields suggests that there must be some competing processes. If the elimination of H or D atoms is the only exit, there should be no isotope effect in yields, since excited triplet states must decompose eventually to eject H(D) atoms. The difference in lifetimes of the triplet states may contribute little to the H(D) production yields. The only candidates for the competition processes are the $H_2$($D_2$) molecular eliminations. The following processes are not only exothermic but also spin-allowed:

$N_2(A)+C_2H_2 \rightarrow N_2+{}^3C_2+H_2+87.0$ kJ mol$^{-1}$ (90.3 kJ mol$^{-1}$ for $C_2D_2$),

$N_2(A)+C_2H_4 \rightarrow N_2+{}^3HCCH+H_2+141.9$ kJ mol$^{-1}$ (130.9 kJ mol$^{-1}$ for $C_2D_4$),

$N_2(A)+C_2H_4 \rightarrow N_2+{}^3H_2CC+H_2+123.7$ kJ mol$^{-1}$ (113.6 kJ mol$^{-1}$ for $C_2D_4$).

The exothermicities are the results from density functional calculations. Of course, D atoms are more likely than H atoms to remain bonded to C atoms and H atoms must be preferentially ejected either as atoms or as molecules. However, the relative importance of the ejection as atoms is less for D atoms and the D-atom yields for deuterated species is less than the H-atom yields for hydrides. Similar situations have been observed in the photodissociation of $C_2H_4$ and $C_2D_4$ by Lin *et al.*[47] who have reported an H/D isotope effect in yields from the photodissociation of ethene at 157 nm. They found that the yield of H atoms for $C_2H_4$ is 0.56, while that of D atoms for $C_2D_4$ is 0.40.[47] Their results have been supported by RRKM calculations from Chang *et al.*, who have shown that the H-atom yield in the 157-nm photodissociation of $C_2H_4$ is 17% larger than the D-atom yield for $C_2D_4$.[48] The isotope effect in the 193-nm photodissociation has been shown to be still larger, 39%.[48] Wang *et al.* have also shown that the H-atom yield in the 121.6-nm photodissociation of $CH_4$ is larger than the sum of the H- and D-atom yields for $CHD_3$.[49,50] These isotope effects have been explained by the competition with the molecular elimination processes. The situation must be similar in the present systems. In H(D)-atom ejection, the transition states must be loose, because the products are two radical species and no large activation barriers are expected. On the other hand, in $H_2(D_2)$ molecular elimination, the transition states may be tight. Then, in the atom ejection processes, the effect of the difference in the zero point energies of the reactant molecules may be more critical and the isotope effect can be larger.

## V. CONCLUSIONS

The H(D)-atom yields in the reactions of $N_2(A\ ^3\Sigma_u^+)$ with $C_2H_2$, $C_2H_4$, and their deuterated variants are less than unity and fairly large H/D isotope effects were observed, although the isotope effects in overall rate constants are minor. These results show that molecular elimination processes are more dominant for deuterated species. The transition states for molecular elimination must be tight while those for atomic ejection must be loose, and the effect of the difference in zero point energies is larger in atom ejection processes.

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TABLE I. Rate constants for the quenching of $N_2(A)$ in units of $10^{-11}$ $cm^3$ $s^{-1}$. The error limits are standard deviations.

| Quencher | Rate constant | Literature values |
|---|---|---|
| $C_2H_2$ | 14.0±0.2 | 16[a], 25[b], 16[c], 20[d] |
| $C_2D_2$ | 14.5±0.3 | |
| $C_2H_4$ | 9.7±0.4 | 15[a], 16[b], 11[c], 14[e], 6[f], 12[g], 10[h], 12[i] |
| $C_2D_4$ | 9.3±0.4 | |
| $NH_3$ | 12.4±0.5 | 16[b], <2[c], 8[d], 17[j], 13[k], 8[l], 14[m] |
| $ND_3$ | 12.1±0.6 | |

[a] Young *et al.* (Ref. 24).

[b] Meyer *et al.* (Ref. 25).

[c] Callear and Wood (Ref. 26).

[d] Bohmer and Hack (Ref. 27).

[e] Taylor and Setser (Ref. 28).

[f] Dreyer and Perner (Ref. 29).

[g] Clark and Setser (Ref. 30).

[h] Thomas *et al.* (Ref. 31).

[i] Ho and Golde (Ref. 32).

[j] Meyer *et al.* (Ref. 33).

[k] Slanger *et al.* (Ref. 34).

[l] Dreyer *et al.* (Ref. 35).

[m] Hack *et al.* (Ref. 11).

TABLE II. H(D)-atom yields in the quenching of $N_2(A)$.

| Reactant | H(D)-atom yield |
|---|---|
| $NH_3$ | $0.9^{a,b}$ |
| $ND_3$ | $0.9^{c}$ |
| $C_2H_2$ | $0.52 \pm 0.07$ |
| $C_2D_2$ | $0.33 \pm 0.06$ |
| $C_2H_4$ | $0.30 \pm 0.05$ |
| $C_2D_4$ | $0.13 \pm 0.03$ |

[a] Tao *et al.* (Ref. 10).

[b] Hack *et al.* (Ref. 11).

[c] Assumed to be the same as $NH_3$.

## Figure Captions

FIG. 1. Reciprocal time constants for the decay of the NO(A-X) emission in Xe/$N_2$/NO/$C_2H_2$ (open circles) and Xe/$N_2$/NO/$C_2H_4$ (closed circles) systems as a function of $C_2H_2$ or $C_2H_4$ pressure. The pressures of Xe, $N_2$, and NO were 267 Pa, 2.67 kPa, and 1.3 Pa, respectively.

FIG. 2. Vacuum-ultraviolet laser-induced fluorescence spectra of H and D atoms measured in the (a) Xe/$NH_3$/$C_2D_2$/$N_2$, (b) Xe/$C_2H_2$/$C_2D_2$/$N_2$, and (c) Xe/$C_2H_4$/$C_2D_2$/$N_2$ systems. The pump-probe delay was 10 μs. The partial pressures of Xe, $NH_3$, $C_2D_2$, $C_2H_2$, $C_2H_4$, and $N_2$ were 667 Pa, 1.3 Pa, 1.3 Pa, 1.3 Pa, 1.3 Pa, and 13.3 kPa, respectively. The vertical scales were adjusted to give the same integrated intensities for the D-atom signals.

FIG. 3. Pump-probe delay time dependence of the D-atom density in the presence of 667 Pa of Xe, 1.3 Pa of $C_2D_2$, and 13.3 kPa of $N_2$. The solid line represents the experimental result, while the dashed lines represent the calculated profile based on the rate constant listed in Table I.

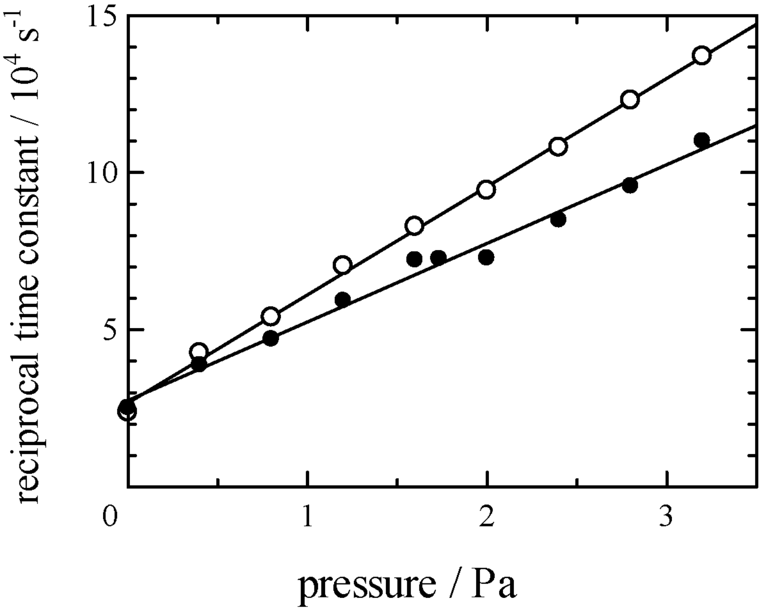

FIG. 1. H. Umemoto

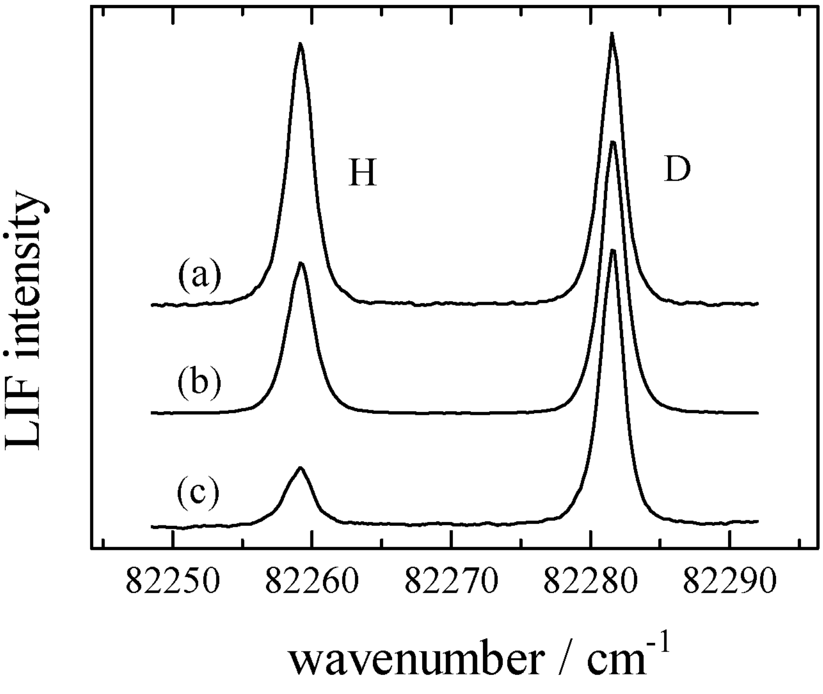

FIG. 2. H. Umemoto

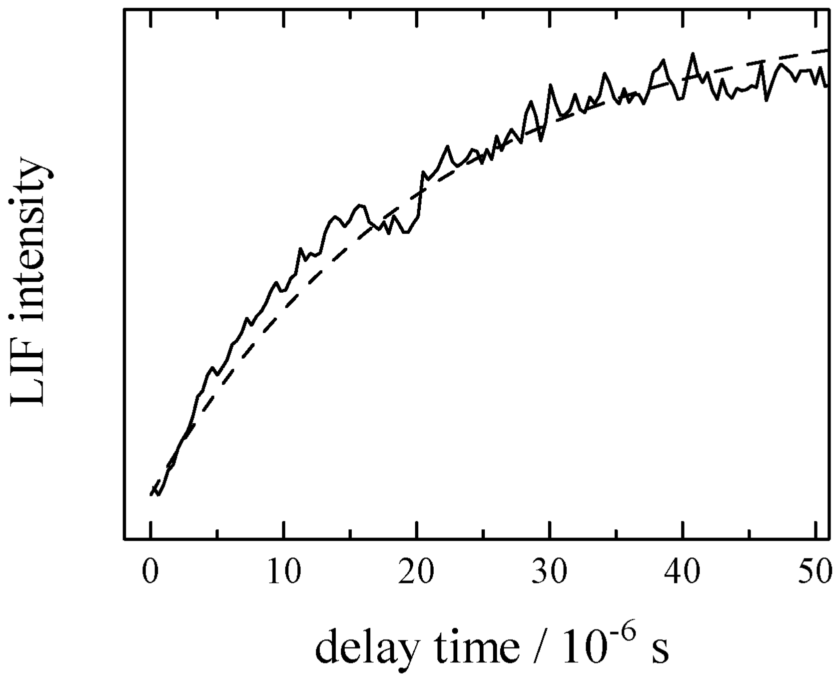

FIG. 3. H. Umemoto