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メタデータ	言語: en 出版者: American Institute of Physics 公開日: 2008-01-30 キーワード (Ja): キーワード (En): 作成者: Umemoto, Hironobu メールアドレス: 所属:
URL	http://hdl.handle.net/10297/504

H(D)-atom yields in the quenching of Xe(6s[3/2]₁) by methane, ethane, ethene, ethyne, and their deuterated isotopologues

Hironobu Umemoto^{a)}

Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu, Shizuoka 432-8561, Japan

^{a)} Electronic mail: thumemo@ipc.shizuoka.ac.jp

The yields for the production of H(D) atoms in the reactions of Xe(6s[3/2]₁) with simple hydrocarbons and their deuterated variants were determined. 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 using a vacuum-ultraviolet laser-induced fluorescence (LIF) technique. 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 profile measurements of the resonance fluorescence from Xe(6s[3/2]₁). H/D isotope effects were observed not only in the overall rate constants, but also in the H(D)-atom yields. The yields for CH₄, C₂H₄, and C₂H₂ were determined to be 0.89, 1.43, 1.03, respectively, while those for CD₄, C₂D₄, and C₂D₂ were found to be smaller; 0.63, 0.86, and 0.79, respectively. The H/D yield ratio for CH₂D₂ was 1.76. The presence of the isotope effects both in the rate constants and the yields suggests that electronic-to-electronic energy transfer processes and abstractive processes are competing.

I. INTRODUCTION

Recently, we have reported that the production yield of D atoms in the reaction of $N_2(a' \ ^1\Sigma_u^+)$, the lowest singlet excited state of N_2 , with CH_2D_2 coincides with that of H atoms within the error limit.¹ This is in contrast to the general tendency of direct vacuum ultraviolet (VUV) photodissociation of partially deuterated hydrocarbons.²⁻⁷ The H-atom yields are much larger in direct photolysis. For example, the H/D production ratio in the photodissociation of CH_2D_2 at 121.6 nm, Lyman- α , has been reported to be between 1.6 and 4.0.²⁻⁴ The absence of an isotope effect in the reaction of $N_2(a')$ has been attributed to the formation of bound HNNCHD₂- and DNNCH₂D-type intermediate complexes, which decompose to $H+N_2+CHD_2$ and $D+N_2+CH_2D$, respectively, with unit probabilities. The electronic energy of $N_2(a')$, 815 kJ mol⁻¹, may be too small to cause the direct energy transfer. Lyman- α corresponds to the energy of 984 kJ mol⁻¹. Since the electronic energy of $Xe(6s[3/2]_1)$, 814 kJ mol⁻¹, is very similar to that for $N_2(a')$, it is interesting to check for the presence or absence of isotope effects in the reactions of $Xe(6s[3/2]_1)$.

Alekseev and Setser have shown that two-photon driven amplified spontaneous emission from $Xe(6p[1/2]_0)$ provides an excellent time-resolved source for the $Xe(6s[3/2]_1)$ resonance state.⁸ This technique is both simple and efficient. The present author has already employed this technique and found that it is not necessary to focus the laser beam to cause the two-photon process.⁹ Alekseev and Setser have determined the rate constants for the quenching of $Xe(6s[3/2]_1)$ by various molecules.⁸ However, they paid less attention to the identification of the reaction products. The determination of the H-atom yields in the deactivation of metastable $Xe(6s[3/2]_2)$ and $Xe(6s'[1/2]_0)$ was reported by Balamuta et al.,¹⁰ who produced these metastable states by electric discharges and detected the H atoms by resonance fluorescence. They determined the yields for

CH₄ and C₂H₆ to be almost unity, but they have not reported on the H/D isotope effect.

In the present work, the yields for the production of H(D) atoms in the reactions of Xe(6s[3/2]₁) with simple hydrocarbons were determined, paying special attention to the H/D isotope effect. The rate constants for the overall quenching were also determined.

II. EXPERIMENT

The experimental apparatus and the procedure were similar to those described elsewhere.⁹ The frequency-doubled output of a dye laser (Lambda Physik, LPD3000E) pumped with a Q-switched Nd:YAG laser (Quanta-Ray, GCR-170) 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 Xe(6s[3/2]₁) was confirmed by resonance fluorescence at 147.0 nm. The overall rate constants for the quenching of this state can be determined from the quencher pressure dependence of the temporal profiles of this vacuum ultraviolet (VUV) emission. A solar-blind photomultiplier tube (Hamamatsu, R6835) was used to monitor the VUV emission. An MgF₂ lens and an interference filter (Acton Research, 145-N) were used to collimate and isolate the resonance fluorescence. The inside of the photomultiplier housing was flushed with dry nitrogen flow. The photomultiplier signal was processed with a digital oscilloscope (LeCroy, 6051A).

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 2²P_J states by a VUV laser pulse at 121.6 (121.5) nm, Lyman- α . The typical delay time

between the pump and probe laser pulses was 3 μ s. The procedures to produce Lyman- α radiation were similar to those described elsewhere.^{11,12} The output of the dye laser around 729.6 nm was doubled in frequency by a KDP (KH₂PO₄) 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 53 kPa, respectively, while the laser pulse energy at the doubled stage was 3 mJ. The doubled output around 364.8 nm was focussed into the tripling cell, 15 cm in length, by a 120 mm focal-length lens. The resulted VUV light was collimated with an MgF₂ lens and entered the reaction vessel. The induced fluorescence was detected at an angle perpendicular to the laser beam with a solar-blind photomultiplier tube (Hamamatsu Photonics, R6835) through an MgF₂ collimating lens and an interference filter (Acton Research, 122-N). The photomultiplier signal was processed with a boxcar averager-gated integrator system (Stanford Research Systems SR240/SR250/SR280) and a computer.

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, 15 cm in length, with an MgF₂ window was attached to the end of the reaction vessel and filled with 130 Pa of NO. The NO⁺ ions produced by the VUV laser radiation were collected by parallel electrodes and the ion current was measured with the boxcar averager-gated integrator system. All the measurements were carried out at 293 \pm 3 K.

H₂ (Takachiho, 99.99995%), D₂ (Sumitomo Seika, isotopic purity 99.5%), NO (Nihon Sanso, 99%), CH₄ (Nihon Sanso, 99.999%), CD₄ (Isotec, isotopic purity 99%), CH₂D₂ (Isotec, isotopic purity 98%), C₂H₆ (Takachiho, 99.9%), C₂H₄ (Sumitomo Seika, 99.9%), He (Teisan, 99.995%), Ar (Nihon Sanso, 99.999%), Kr (Nihon Sanso, 99.995%), and Xe (Teisan, 99.995%) were used from cylinders without further purification. C₂D₄

was the product of ICON Stable Isotopes (isotopic purity 99 %). C_2H_2 (C_2D_2) was synthesized from CaC_2 (Katayama Kagaku) and H_2O (D_2O).¹³ D_2O was the product of Aldrich (isotopic purity 99.9 %).

III. RESULTS

A. Quenching of $Xe(6s[3/2]_1)$

The experimental conditions for the decay profile measurements of the fluorescence from $Xe(6s[3/2]_1)$ were the same as those described previously.⁹ The Xe pressure was 267 Pa while the total pressure was kept constant at 13.3 kPa by adding He. The decay profiles were single exponential under these conditions. The reciprocal time constant for the decay increased linearly with the quencher pressure. The results for C_2H_2 and C_2D_2 are shown in Fig. 1. It is possible to evaluate the rate constants for the quenching of $Xe(6s[3/2]_1)$ from these slopes. The rate constants for H_2 , D_2 , CH_4 , C_2H_6 , and C_2H_4 have been reported in a previous publication.⁹ In the present work, the author checked the former results and found that the previous values are correct except for D_2 . As for D_2 , the previous value was found to be 17 % smaller. The correct value for D_2 is listed in Table I, together with the new results for CH_2D_2 , CD_4 , C_2D_4 , C_2H_2 , and C_2D_2 . The error limits are the standard deviations. Literature values are also included.^{8,14,15}

B. H(D)-atom yields

In the H-atom yield measurements for hydride species, the laser-induced fluorescence spectra for H and D atoms were recorded for $Xe/H_2/D_2/He$ and $Xe/hydride/D_2/He$ systems. Typical LIF spectra for the $Xe/H_2/D_2/He$, $Xe/C_2H_4/D_2/He$, and $Xe/CH_4/D_2/He$ systems are shown in Fig. 2. The pressures of Xe, H_2 , and D_2 were kept constant, 267, 133, and 133 Pa, respectively. The hydride pressure was chosen to

satisfy $k_{H_2}[H_2]=k_{RH}[RH]$, where k_{H_2} and k_{RH} are the overall rate constants for the quenching of $Xe(6s[3/2]_1)$ by H_2 and the hydride, while $[H_2]$ and $[RH]$ are their pressures. In these systems, the D-atom signal can be used as an internal standard and the ratio of the H/D signal ratios can be correlated directly to the quantum yield for the production of H atoms for the hydride molecules, since the yield for the production of H atoms from H_2 can be assumed to be two, as for the reactions of triplet-state metastable Xe atoms.¹⁰ The quenching processes of $H(2^2P_1)$ and $D(2^2P_1)$ were not taken into account although the rate constant for the quenching of $H(2^2P_1)$ by H_2 has been reported to be large and there may be an isotope effect in the rate constants.¹⁶ The unimportance of the effect of the quenching of $H(2^2P_1)$ and $D(2^2P_1)$ was checked by changing the H_2 and D_2 pressures. There was no change in the signal intensity ratios when the pressures were halved. He was added to induce pressure broadening and consequently to increase the signal intensity. The diffusional loss of H(D) atoms was minor even in the absence of He. This was confirmed by measuring the H(D)-atom signal intensity as a function of pump-probe delay time. There was no change when the delay time was changed between 2 and 6 μ s. No change was observed either, in the H/D ratio, when the He pressure was changed between 0.8 and 6.1 kPa. No H-atom signals were observed in the absence of hydride molecules or in the absence of the pump laser. The latter shows that the photodissociation of the hydride species by the probe laser is negligible. It should be noted that the signal intensities for H and D atoms cannot be compared directly because the VUV laser intensity depends on the wavelength. The change in the VUV radiation produced by the tripling by Kr can be determined by detecting the product H and D atoms in a 1:1 mixture of H_2 and D_2 . As can be seen in Fig. 2, there was no change in the signal intensities; the ratio was 1.00 ± 0.02 , although the rate constant for the quenching by H_2 is 1.37 times larger than that by D_2 . Then, the VUV intensity at 121.53nm,

Lyman- α (D), must have been 37 % more intense than that at 121.57 nm, Lyman- α (H). This variation in the VUV intensity can be reduced by adjusting the Kr/Ar pressures, but the conversion efficiency may become lower.¹⁷

Similar measurements were carried out to determine the D-atom yields for deuteride species. The LIF spectra for H and D atoms were recorded for Xe/H₂/D₂/He and Xe/H₂/deuteride/He systems. The deuteride pressure, [RD], was chosen to satisfy $k_{D_2}[D_2]=k_{RD}[RD]$.

Here, two corrections are necessary. The first one is caused by the difference in the absorption coefficients at Lyman- α (H) and Lyman- α (D). Organic molecules may absorb Lyman- α radiation to reduce the LIF intensity. When the absorption coefficient depends on the wavelength, a correction is necessary. The absorption coefficients were evaluated from the transmitted VUV laser intensity measured by the NO⁺ ion current. The absorption coefficients at Lyman- α (H) and Lyman- α (D) by C₂H₂ were determined to be 2010 and 1600 atm⁻¹cm⁻¹, respectively (1 atm = 1.013 × 10⁵ Pa). The path length of the LIF detection was 14 cm, while the C₂H₂ pressure was 1.4 Pa. Then, the correction factor should be 1.08. The absorption coefficients at Lyman- α (H) and Lyman- α (D) by C₂H₄ were determined to be 810 and 750 atm⁻¹cm⁻¹, respectively. The corresponding correction factor should be 1.01 in the presence of 1.2 Pa of C₂H₄. No corrections are necessary for other quenchers. For example, the absorption coefficients by C₂D₄ are similar to those by C₂H₄, but the difference between Lyman- α (H) and Lyman- α (D) is only 10 atm⁻¹cm⁻¹. The absorption coefficients by C₂D₂ are much smaller than those by C₂H₂; 90 and 110 atm⁻¹cm⁻¹, respectively, at Lyman- α (H) and Lyman- α (D). It should be noted that Lyman- α (H, D) coincides with the absorption at the 4R''2¹₀ transition of C₂H₂ but with none of the transitions for C₂D₂.¹⁸

The second correction is related to the quenching of Xe(6p[1/2]₀) by H₂ and D₂.

No quenching of ASE was observed under the present experimental conditions,⁹ but this does not necessarily exclude the possible quenching of Xe(6p[1/2]₀) after the termination of the laser pulse. The radiative lifetime of Xe(6p[1/2]₀), 26.8 ns, is longer than the laser pulse duration.¹⁹ In order to estimate this contribution, the change in the peak intensity of the 147-nm emission was measured; it decreased by 2.5 % when 133 Pa of H₂ was introduced. As will be shown in the Appendix, this decrease leads to the correction factor of 1.07. When 133 Pa of D₂ was introduced, the 147-nm emission peak intensity decreased by 1.5%. The correction factor for D₂-added systems is 1.06.

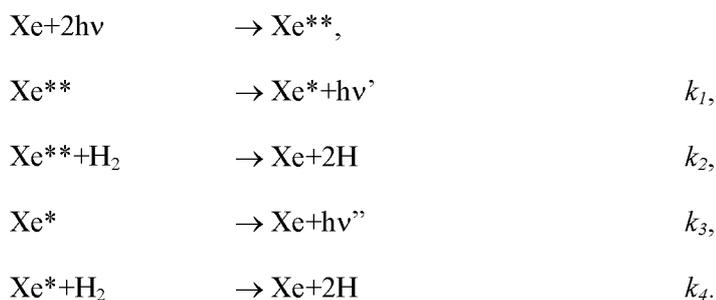
No other corrections are necessary. The reaction rates of H atoms with RH(RD), such as C₂H₂ and C₂H₄, are slow enough.^{20,21} The time constant for the reaction of H atoms in the presence of 1.2 Pa of C₂H₄ is 3 ms. It is possible to ignore the production of H atoms by the photodissociation of hydrocarbons through resonance radiation at 147.0 nm. The absorption coefficient of C₂H₄ at 147 nm is 400 atm⁻¹ cm⁻¹,²² which is the largest among the hydrocarbons used. It is difficult to estimate the probe laser beam diameter but that must be less than 1 cm and the absorbance of the resonance fluorescence in the presence of 1.2 Pa of C₂H₄ should be 0.005. In the presence of 1.2 Pa of C₂H₄ and 133 Pa of D₂, 58 % of Xe(6s[3/2]₁) is quenched. Then, the overestimation of the production yield is only 0.002, which can completely be ignored.

The production yields of H(D) atoms after the corrections are listed in Table I. The yield for C₂H₄ is larger than unity. This suggests that a decomposition to C₂H₂+2H takes place. In direct photolysis, the presence of this channel was proposed as early as in the 1960s.^{22,23} More recently, Lin et al. examined the photolysis processes of C₂H₄ and C₂D₄ at 157 nm, and concluded that this process is more important than the production of H₂C=CH+H.⁷ Lin et al. also presented the energetics of the decomposition processes. They showed that the production of HC≡CH+H₂, H₂C=C+H₂,

$\text{H}_2\text{C}=\text{CH}+\text{H}$, and $\text{HC}\equiv\text{CH}+2\text{H}$ are all exothermic and possible. In addition, the author confirmed by density functional calculations that the production of $\text{H}_2\text{C}=\text{C}(\text{singlet})+2\text{H}$ is 29 kJ mol^{-1} exothermic and energetically possible in the present system, although it is inaccessible in the 157-nm photolysis. The computational procedure of the density functional calculations is similar to that described elsewhere.²⁴

IV. DISCUSSION

Kawasaki et al. examined the $\text{Xe}(6\text{p}[1/2]_0)/\text{H}_2$ system by employing a two-photon excitation technique similar to the present one and concluded that the major precursor of H atoms is $\text{Xe}(6\text{p}[1/2]_0)$ rather than $\text{Xe}(6\text{s}[3/2]_1)$, which is in contradiction to the present scheme.²⁵ However, as was pointed out by Alekseev et al.,²⁶ Kawasaki et al. did not take into account the ASE processes, and this should be the cause of the discrepancy. Kawasaki et al. found that the slope of the Stern-Volmer plot for the infrared (IR) emission from $\text{Xe}(6\text{p}[1/2]_0)$ at 828.0 nm agrees with that for the VUV emission from $\text{Xe}(6\text{s}[3/2]_1)$ at 147.0 nm and demonstrated that the precursor of H atoms is $\text{Xe}(6\text{p}[1/2]_0)$ based on this agreement. The following scheme may be assumed for the Xe/H_2 system.



Here Xe^{**} and Xe^* represent $\text{Xe}(6\text{p}[1/2]_0)$ and $\text{Xe}(6\text{s}[3/2]_1)$, respectively. The rate

constants are represented by k_i . If ASE processes can be ignored, the slope for the Stern-Volmer plot for the integrated IR emission intensity should be k_2/k_1 , while that for VUV should be $(k_2/k_1+k_4/k_3)$. The coincidence of the slopes suggests that $k_2/k_1 \gg k_4/k_3$ and that collisional quenching of Xe(6s[3/2]₁) is minor compared to the radiative decay. However, if we take into account the ASE processes, the situation is different. Since Kawasaki et al. observed the IR emission perpendicular to the laser beam, they must have observed the fluorescence after the laser pulse as well as after ASE terminated. In such a case, their Stern-Volmer analysis for IR emission should be reasonable. However, Xe(6s[3/2]₁) should be produced instantaneously via ASE and the slow rise can be ignored. Then, the slope of the Stern-Volmer plot for VUV should be k_4/k_3 , rather than $(k_2/k_1+k_4/k_3)$. In this case, the coincidence of the slopes of the Stern-Volmer plots for IR and VUV should be fortuitous. The effective radiative lifetime of Xe(6s[3/2]₁) under the conditions of Kawasaki et al. is calculated to be 3.8 μ s, which is not much different from that observed in the present system, 3.5 μ s, and seems to be reasonable in the presence of radiation imprisonment. It should be noted that the rate constant for the quenching of Xe(6p[1/2]₀) determined by Kawasaki et al. is still valid.

The present results on the H/D isotope effects, both in rate constants and quantum yields, can be explained by assuming that not only electronic energy transfer but also abstractive processes are present. Table II summarizes the results. The isotope effects observed in the rate constants are similar to those observed in the quenching of N(2²D) and N(2²P) as is shown in Table III.²⁷⁻³⁰ N(2²D) is known to insert into the C-H bonds of alkane hydrocarbons,³⁵ while addition processes are expected to take place to unsaturated hydrocarbons.²⁹ The problem is that the isotope effect observed in the H(D)-atom yields in methane cannot be explained by an insertion mechanism. In order to explain the small D-atom yield in the CD₄ system by an insertion mechanism, it is

necessary to assume that $D_3C-Xe-D$ complexes decompose efficiently to CD_4+Xe or CD_2+D_2+Xe . Both sound unrealistic. In the latter case, D atoms must migrate more rapidly than H atoms. Besides this, $Xe(6s[3/2]_1)$ must be too large to insert into C-H or C-D bonds. The size of $Xe(6s[3/2]_1)$ must be similar to those of ground-state Cs and excited-state K atoms. It has been demonstrated that $Na(4^2P)$ can insert into H-H bonds, but $K(5^2P)$ cannot because of its large size.^{36,37} In the reactions with unsaturated species, addition-type complexes such as $H_2C(-Xe)-CH_2$ may be produced. $D_2C(-Xe)-CD_2$ may be longer-lived than $H_2C(-Xe)-CH_2$ and collisionally relaxed to $D_2C=CD_2$ and Xe to lower the D-atom yield. However, no He pressure dependence was observed in the H(D)-atom yields between 0.8 and 6.1 kPa. The H/D isotope effects in the rate constants can well be explained by an abstraction mechanism, which may take place for all species examined. The isotope effects can be ascribed to the difference in the zero-point energies of the C-H and C-D bonds. However, the isotope effects in the H(D)-atom yields cannot be explained by an abstraction mechanism. Once XeH or XeD molecules are formed, the H or D atom must be ejected eventually. As was mentioned in the Introduction, still larger isotope effects have been observed in direct photolysis by VUV radiation.²⁻⁷ Molecular elimination is more important in deuterated species.^{3,4,7} The isotope effects in yields observed in the present work can be rationalized if electronically excited species are produced by energy transfer and decomposes spontaneously. However, in such an electronic-to-electronic energy transfer, no large isotope effects are expected in the rate constants. In conclusion, the isotope effects observed in the present system cannot be explained by a single mechanism and at least two processes are competing.

As shown in Table III, large H/D isotope effects, around one order of magnitude, were observed in the quenching of $O_2(b^1\Sigma_g^+)$ and $NH(b^1\Sigma^+)$ by Stuhl and coworkers.³²⁻³⁴

However, the situation is different in these systems. The electronic energies of $O_2(b^1\Sigma_g^+)$ and $NH(b^1\Sigma^+)$ are 158 and 254 kJ mol^{-1} , respectively, which are much smaller than the electronic energies of the lowest excited levels of hydrocarbon species. One of the possible explanations of the large isotope effects is that the quenching proceeds via electronic-to-vibrational energy transfer.³³ In such a case, the quenching rate constant may strongly depend on the vibrational frequencies of the quenching molecules. Of course there remains the possibility for chemical quenching, such as $NH(b)+C_2H_4 \rightarrow NH_2+C_2H_3$.

Finally, Table IV compares the present results for CH_2D_2 with those for the reactions of other excited species and the direct photolysis. The H/D production yield ratios are small for $N(2^2D)$ and $N_2(a')$ and large for $Xe(6s[3/2]_1)$ and direct photolysis. These results are consistent with the above model, namely that direct energy transfer processes play some role in the quenching of $Xe(6s[3/2]_1)$.

V. CONCLUSIONS

The quenching processes of $Xe(6s[3/2]_1)$ by simple hydrocarbons and their deuterated isotopologues were examined. Both the rate constants and the H(D)-atom yields were found to be large, and H/D isotope effects were observed in both the overall rate constants and the yields. These results suggest that not only electronic-to-electronic energy transfer followed by spontaneous decomposition, but also abstractive processes to produce XeH (XeD) are present.

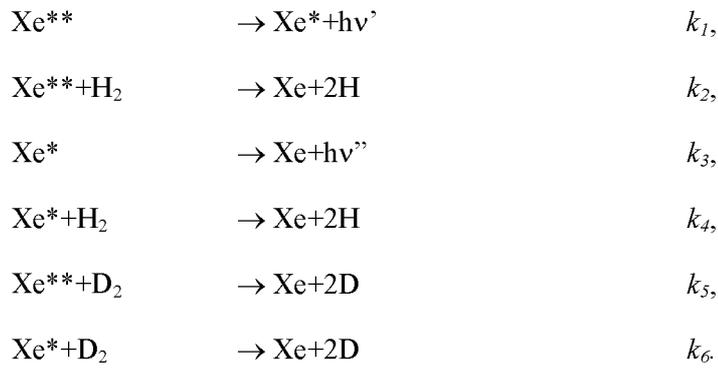
ACKNOWLEDGMENT

This work was partially funded by the Grant-in-Aid for Science Research (No. 17550009) from the Japan Society for the Promotion of Science.

APPENDIX

Evaluation of the correction factor for the direct quenching of Xe(6p[1/2]₀)

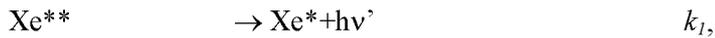
In the Xe/H₂/D₂ system, the production processes of H and D atoms may be represented by the following scheme:

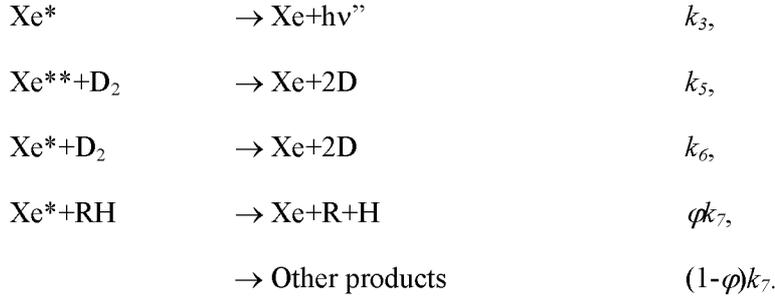


Here, Xe^{**} and Xe^{*} stand for Xe(6p[1/2]₀) and Xe(6s[3/2]₁), respectively, while k_1 represents the radiative decay rate of Xe(6p[1/2]₀) including the effect of ASE. As far as the loss processes of H and D atoms can be ignored, the H/D ratio after a long delay must be:

$$\frac{[\text{H}]}{[\text{D}]} = \frac{k_2[\text{H}_2] + k_4[\text{H}_2] \frac{k_1}{k_3 + k_4[\text{H}_2] + k_6[\text{D}_2]}}{k_5[\text{D}_2] + k_6[\text{D}_2] \frac{k_1}{k_3 + k_4[\text{H}_2] + k_6[\text{D}_2]}}.$$

In the Xe/RH/D₂ system, similar scheme may be considered:





$$\frac{[H]}{[D]} = \frac{\phi k_7 [RH] \frac{k_1}{k_3 + k_6 [D_2] + k_7 [RH]}}{2(k_5 [D_2] + k_6 [D_2]) \frac{k_1}{k_3 + k_6 [D_2] + k_7 [RH]}}.$$

Here, ϕ is the yield to produce H atoms from RH. The quenching process of Xe(6p[1/2]₀) by RH was ignored because the pressure was low. In the present measurements, [RH] was chosen to satisfy $k_4[H_2]=k_7[RH]$, while [D₂] was kept constant at 133 Pa. The H₂ pressure was also 133 Pa. Then, the ratio of the above two [H]/[D] ratios, R , should be represented by

$$R = \frac{\phi k_7 \frac{k_1}{k_3 + k_4 [H_2] + k_6 [D_2]} [RH]}{2(k_2 + k_4 \frac{k_1}{k_3 + k_4 [H_2] + k_6 [D_2]}) [H_2]}.$$

If process 2 can be ignored and $k_2=0$, the value of R agrees with that for simple expectation;

$$R' = \frac{\phi k_7 [RH]}{2k_4 [H_2]}.$$

Now, we would like to evaluate the correction factor, R'/R .

$$\frac{R'}{R} = \frac{k_2 + \frac{k_1 k_4}{k_3 + k_4[\text{H}_2] + k_6[\text{D}_2]}}{\frac{k_1 k_4}{k_3 + k_4[\text{H}_2] + k_6[\text{D}_2]}}.$$

The rate constants k_3 , k_4 , and k_6 have been determined to be $2.9 \times 10^5 \text{ s}^{-1}$, $7.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, and $5.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively, by the present author. Kawasaki et al. have determined the value of k_2 to be $1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The peak height of the 147-nm emission decreased by 2.5 % by the addition of 133 Pa of H_2 . This means that $k_2[\text{H}_2]=0.025k_1$ and that $k_1=1.3 \times 10^9 \text{ s}^{-1}$. When we substitute these values, we obtain the correction factor, R'/R , of 1.07. Similar correction factors can be obtained in the deuterated systems.

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TABLE I. Rate constants for the quenching of Xe(6s[3/2]₁) in units of $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and the H(D)-atom yields.

Reactant	Rate constant		H(D)-atom yield
	Present work	Literature values	
H ₂	0.74 ± 0.01	0.86^a	2^d
D ₂	0.54 ± 0.01	0.47^a	2^d
CH ₄	34.3 ± 1.1	33^b	0.89 ± 0.07
CD ₄	22.3 ± 0.3		0.63 ± 0.06
C ₂ H ₆	64.5 ± 2.7	61^c	0.83 ± 0.08
C ₂ H ₄	79.9 ± 1.9		1.43 ± 0.13
C ₂ D ₄	71.0 ± 2.0		0.86 ± 0.09
C ₂ H ₂	70.4 ± 1.8	75^b	1.03 ± 0.10
C ₂ D ₂	57.1 ± 1.0		0.79 ± 0.07
CH ₂ D ₂	27.3 ± 0.9		1.76 ± 0.15 (H/D ratio)

^a Kanaev¹⁴.

^b Alekseev⁸.

^c Alekseev¹⁵.

^d The yield for H₂(D₂) was assumed to be 2.

TABLE II. Ratios of the rate constants for the quenching of $\text{Xe}(6s[3/2]_1)$ by hydrocarbons to those of fully deuterated isotopologues and the ratios of H(D)-atom yields.

Reactant	Rate constant	H(D)-atom yield
Methane	1.54 ± 0.07	1.41 ± 0.25
Ethene	1.13 ± 0.06	1.66 ± 0.32
Ethyne	1.23 ± 0.05	1.30 ± 0.24

TABLE III. Ratios of the quenching rate constants by hydrocarbons to those of fully deuterated isotopologues at room temperature.

Reactant	Xe(6s[3/2] ₁) ^a	N(² D)	N(² P)	N ₂ (a') ^f	N ₂ (A) ^g	NO(A) ^h	NH(b) ⁱ	O ₂ (b)
Methane	1.54	1.7 ^b 1.8 ^c	1.5 ^c	1.1			5.8	1.4 ^j
Ethene	1.13	1.2 ^d	1.1 ^d		1.0	1.1	10.8	3.1 ^k
Ethyne	1.23	1.1 ^e	1.1 ^e		1.0	1.0	4.6	5.5 ^k

^a Present work.

^b Umemoto²⁷.

^c Takayagnagi²⁸.

^d Sato²⁹.

^e Takayanagi³⁰.

^f Umemoto¹.

^g Umemoto³¹.

^h Umemoto¹³.

ⁱ Zetzsch³².

^j Kohse-Höinghaus³³.

^k Stuhl³⁴.

TABLE IV. H/D production yield ratios for CH₂D₂.

Reactant	Xe(6s[3/2] ₁) ^a	N(² D) ^b	N ₂ (a') ^c	O(¹ D) ^d	Lyman- α photolysis
	1.76	1.1	1.1	1.29	3.5 ^e
					4.0 ^f
					1.6 ^g

^a Present work.

^b Umemoto³⁵.

^c Umemoto¹.

^d Satyapal³⁸.

^e Heck².

^f Wang³.

^g Wang⁴.

Figure Captions

FIG. 1. Reciprocal time constants for the decay of the resonance fluorescence of $\text{Xe}(6s[3/2]_1)$ at 147.0 nm in $\text{Xe}/\text{C}_2\text{H}_2/\text{He}$ (open circles) and $\text{Xe}/\text{C}_2\text{D}_2/\text{He}$ (closed circles) systems as a function of ethyne pressure. The Xe pressure was 267 Pa, while the total pressure was 13.3 kPa.

FIG. 2. Vacuum-ultraviolet laser-induced fluorescence spectra of H and D atoms measured in the (a) $\text{Xe}/\text{H}_2/\text{D}_2/\text{He}$, (b) $\text{Xe}/\text{C}_2\text{H}_4/\text{D}_2/\text{He}$, and (c) $\text{Xe}/\text{CH}_4/\text{D}_2/\text{He}$ systems. The pump-probe delay was 3 μs . The partial pressures of Xe, H_2 , D_2 , C_2H_4 , CH_4 , and He were 267, 133, 133, 1.2, 2.9, and 800 Pa, respectively. The vertical scales were adjusted to give the same integrated intensities for the D-atom signals.

FIG. 3. Vacuum-ultraviolet laser-induced fluorescence spectra of H and D atoms measured in the $\text{Xe}/\text{CH}_2\text{D}_2/\text{He}$ system. The pump-probe delay was 3 μs . The partial pressures of Xe, CH_2D_2 , and He were 266, 6.7, and 800 Pa, respectively.

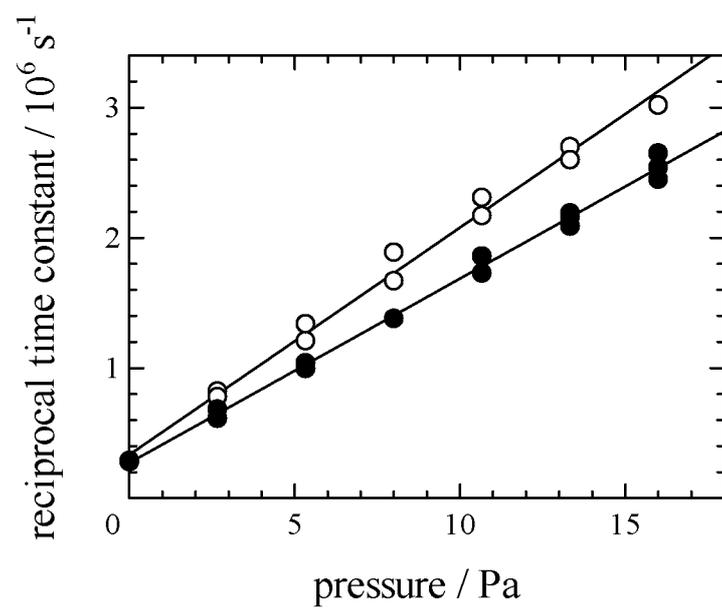


Fig. 1 Umemoto

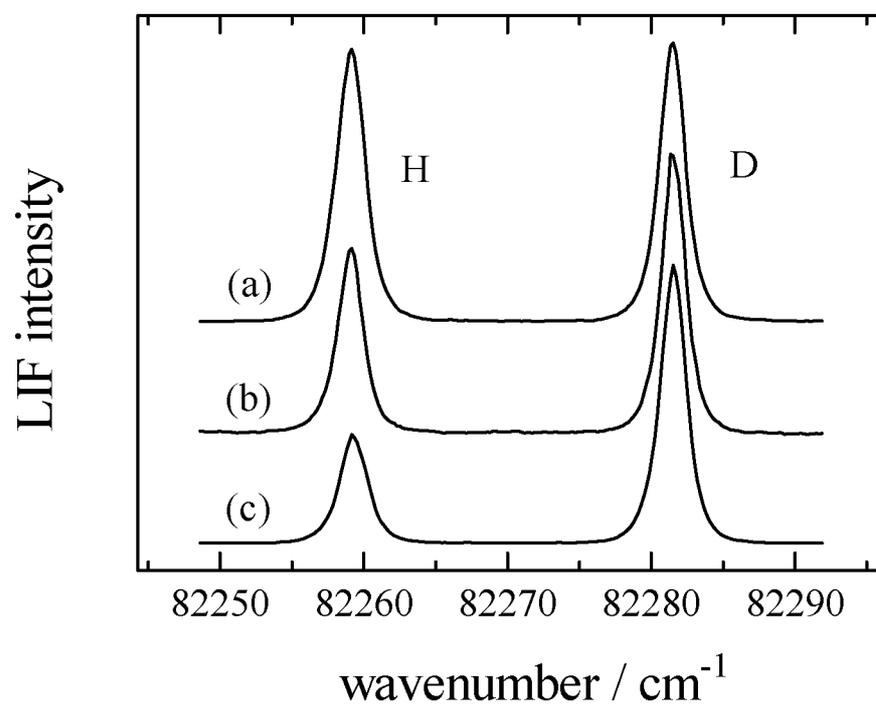


Fig. 2 Umemoto

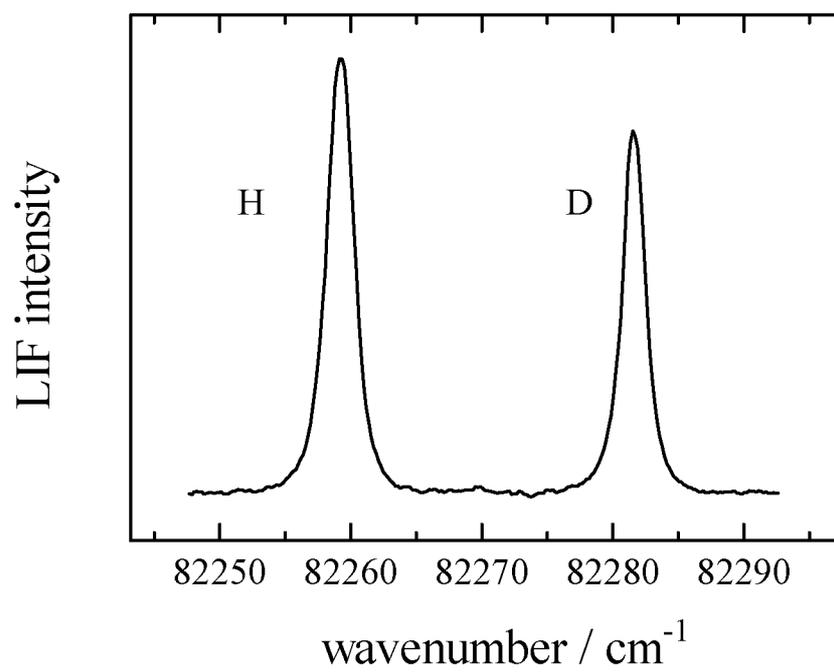


Fig. 3 Umemoto