NASCENT VIBRATIONAL STATE DISTRIBUTIONS OF ZnH(\(X^2\Sigma^+\)) AND ZnD(\(X^2\Sigma^+\)) PRODUCED IN THE REACTIONS OF Zn(\(4^1P_1\)) WITH H\(_2\) AND D\(_2\)

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The reactions of Zn(\(4^1P_1\)) with H\(_2\) and D\(_2\) were studied by employing a laser pump-and-probe technique. The nascent vibrational state distributions of ZnH(\(X^2\Sigma^+\)) and ZnD(\(X^2\Sigma^+\)) were determined. The distributions were much cooler than the statistically expected ones. These results are consistent with the insertive attack model proposed for other excited metal-H\(_2\) systems. The quantum yield for the production of ZnH(\(X^2\Sigma^+\)) was measured to be low; around 0.5 of that for CH\(_4\). Three-body dissociation processes to produce Zn(\(4^3S_0\)) + H + H must be more dominant than the production of ZnH.

KEY WORDS: Zn, ZnH, ZnD, Excited state, Nascent state distribution

INTRODUCTION

Since the pioneering work by Polanyi and coworkers, the determination of the nascent quantum state distribution of reaction products has been one of the major subjects in the field of reaction dynamics.\(^1\) Tsuchiya and coworkers measured the nascent vibrational distributions of CO and NO molecules in the mercury photosensitized reactions.\(^2,3\) They concluded that the vibrational distributions are in general agreement with the forced oscillator half-collision model, while statistical prior distributions are far from the experimental results.

In the reactions of excited group 2 and 12 metal atoms with hydrogen molecules, there have been many experimental studies in which the nascent rotational state
distributions of the metal hydride molecules were determined. It has been shown that Cd(5^3P), Zn(4^3P), Mg(3^1P) and Hg(6^3P) atoms insert into the H–H bond to produce rotationally excited metal hydride molecules. On the other hand, there have been less studies on the determination of the vibrational state distributions. In the quenching of Cd(5^3P) by H_2, only vibrationally ground state CdH can be produced energetically. In the quenching of Zn(4^3P), vibrational states only up to \( v'' = 2 \) are possible. On the other hand, as for Zn(4^1P), vibrational levels up to the dissociation limit, \( v'' = 5 \), are energetically possible. In such a case, determination of the vibrational state distribution is informative.

In the quenching of excited Hg(6^3P), HgH molecules up to \( v'' = 2 \) have been identified. Bras and coworkers measured both the rotational and vibrational state distributions of HgH(X^2Σ^+ ) and HgD(X^2Σ^+ ) produced in the reactions of Hg(6^3P) and isotopic hydrogens. They found that the vibrational population decreases monotonously with the increase in the vibrational energy. The production of HgH and HgD was first established by Callear and coworkers. They determined the quantum yields of HgH and HgD. Recently, Yi et al. have investigated the same system by monitoring H and D atoms. The results obtained by Callear and coworkers were generally confirmed.

Recently, we have determined the nascent rotational and vibrational state distributions of ZnH(X^2Σ^+ ) produced in the reaction of Zn(4^3P) with H_2O and alkane hydrocarbons. The results for H_2O suggest an abstraction mechanism of an H atom through a Zn–H–OH intermediate. On the other hand, it was suggested that the reactions with alkane hydrocarbons proceed with insertive long-lived intermediate complexes. In the present work, the nascent vibrational state distributions of ZnH(X^2Σ^+ ) and ZnD(X^2Σ^+ ) produced in the following reactions:

\[
\text{Zn}(4^1P) + H_2 \rightarrow \text{ZnH}(X^2Σ^+) + H + 209 \text{ kJ mol}^{-1},
\]
\[
\text{Zn}(4^1P) + D_2 \rightarrow \text{ZnD}(X^2Σ^+) + D + 204 \text{ kJ mol}^{-1},
\]

were measured. The results were compared with those for other excited metal atoms as well as the statistical distributions.

EXPERIMENTAL

A standard pump-and-probe technique was employed. Zn vapor in a heat pipe oven was excited to the 4^1P state with an output of a dye laser, the wavelength of which was tuned to the Zn(4^1P \rightarrow 4^1S_0) resonance transition at 213.9 nm. The product ZnH(ZnD) was probed through laser-induced fluorescence by using another dye laser after a short time delay. The vibrational distribution was derived from the LIF spectra obtained under rotationally relaxed but vibrationally near nascent conditions.

The LIF spectra were typically recorded in the presence of 20 kPa of Ar and 260 Pa of H_2(D_2). The pump-probe delay time was typically 100 ns. Under such conditions, ZnH(ZnD) molecules are rotationally relaxed, while vibrational relaxation is still minor. The absence of vibrational relaxation was checked by changing the gas pressures as well as the delay time. The total pressure was changed between
20 kPa and 29 kPa, while the delay time was changed between 100 ns and 200 ns. No marked change was observed in the LIF spectra. The detection was achieved by using the $\Delta \nu = -1$ sequence of the $A \ ^{2}\Pi \leftarrow X \ ^{2}\Sigma^+$ transition for the $\nu'' = 1, 2$ and 3 vibrational levels and the $\Delta \nu = 0$ sequence for $\nu'' = 0$. The scanning region was 430 nm–462 nm for ZnH and 431 nm–453 nm for ZnD. A XeCl laser (Lambda Physik, EMG50) pumped dye laser (Lambda Physik, FL2002) was used as a pump laser. A nitrogen laser (Laser Photonics, UV14) pumped dye laser (Laser Photonics, DL14) was used as a probe laser. The pump and probe laser beams were aligned collinearly. The LIF signals from the reaction system were collected at the right angle to the laser axis. A combination of convex lenses was used to focus the laser-induced fluorescence onto a photomultiplier tube (Hamamatsu Photonics, R212UH). The resonance fluorescence from Zn(4P) was removed by a cutoff filter (Toshiba UV37). The LIF signals were processed with a digital boxcar integrator (NF Circuit Design, BX-531/BP-10) and a computer (NEC, PC9801). The two lasers and the detection system were synchronized by using a common delay/pulse generator (Stanford Research Systems, DG535). The temperature of the reaction zone was measured to be 700 K.

Zn (Aldrich 99.9999%), H$_2$ (Showa Denko, 99.99%), D$_2$ (Showa Denko, isotopic purity 99.5%), Ar (Toyo Sanso, 99.9995%) and CH$_4$ (Nihon Sanso) were used without further purification.

RESULTS

Figure 1 shows the rotationally relaxed but vibrationally unrelaxed LIF spectrum of ZnH($A \ ^{2}\Pi, \nu' \leftarrow X \ ^{2}\Sigma^+$, $\nu''$) obtained in the presence of H$_2$. The observed bands are (0,0), (2,3), (1,2) and (0,1) bands. The (0,3) band of the B–X transition was also observed. Only the $P_{12}$ branch is shown for the (0,0) band, while main branches are shown for other bands. The vibrational distribution of ZnH($X \ ^{2}\Sigma^+$) was determined by comparing the experimental spectrum with the simulated one. The simulation procedure was the same as that described previously. The term values of ZnH($X \ ^{2}\Sigma^+$) and ZnH($B \ ^{2}\Pi$) as well as ZnH($B \ ^{2}\Sigma^+$) have been reported by Stenvinkel.6 The Franck-Condon factors calculated by Nicholls were employed.17 The Hönl-London factors were calculated in accordance with the equations presented by Earls.18 As for the B–X transition, the Hönl-London factors can be evaluated by the equations in Ref. 19. The Franck-Condon factors for the B–X transition have been presented by Balfour et al.20 The rotational distributions for all the vibrational levels could be reproduced by a Boltzmann distribution at 750 K. The vibrational distributions which give the best fit to the experimental results are listed in Table 1. The simulated spectrum obtained by assuming the above rotational and vibrational distributions is shown in Figure 2. The error limits in the relative vibrational populations are 10 or 20%. The error limits are larger for higher levels. Similar results were obtained for D$_2$. The term values as well as the Franck-Condon factors for the ZnD(A–X) transition have been presented by Balfour and Taylor.21 The H/D isotope effect is not clear in the vibrational state distributions as well as in the vibrational energy dis-
tributions considering the present experimental uncertainties. The best-fit vibrational temperature for ZnH is calculated to be 4000 K, while that for ZnD is 3700 K. The prior and the phase-space distributions are also listed in Table 1.22

Table 1 Vibrational state distributions of ZnH($^3\Sigma^+$) and ZnD($^3\Sigma^+$) produced in the reactions of Zn($^4P_1$) with $H_2$ and $D_2$

|        | $v'' = 0$ | $v'' = 1$ | $v'' = 2$ | $v'' = 3$ |
|--------|-----------|-----------|-----------|-----------|
| ZnH    | experimental | 1.0 | 0.6 | 0.5 | 0.2 |
|        | prior | 1.00 | 0.80 | 0.63 | 0.44 |
|        | phase-space | 1.00 | 0.85 | 0.71 | 0.53 |
| ZnD    | experimental | 1.0 | 0.6 | 0.4 | 0.3 |
|        | prior | 1.00 | 0.86 | 0.73 | 0.58 |
|        | phase-space | 1.00 | 0.90 | 0.80 | 0.67 |

The relative quantum yield for the production of ZnH was determined by measuring the LIF signal intensities of the $^3P_2$ branch of the (0,0) band after the rotational relaxation as well as the production of ZnH was accomplished. The procedure was similar to that employed in our previous work on $H_2O$.14 $CH_4$ was used as a standard. The partial pressures of $H_2$ and $CH_4$ were adjusted so that the temporal profiles of the resonance fluorescence from Zn($^4P_1$) were the same. It can be shown that the
relative yield is given by the ratio of the LIF intensities. Although the decay profile of the fluorescence was not exactly exponential because of radiation imprisonment, this non-exponentiality cancels by measuring the relative LIF intensities under the above conditions. The yield for H₂ relative to that for CH₄ was determined to be 0.50 ± 0.05.

From the vibrational distribution obtained above, the ratio of the vibrational energy of ZnH to the total available energy, \( f_v \), was calculated to be 0.07 when we ignore the population over \( v'' = 4 \). If we extrapolate the distribution over \( v'' = 4 \) by using the vibrational temperature for \( v'' \leq 3 \) levels, \( f_v \) becomes 0.08. The value of \( f_v \) for ZnD was calculated to be 0.06 when the population over the \( v'' = 4 \) levels were ignored. If we include the population of the \( v'' = 4 \) and \( v'' = 5 \) levels by extrapolation, \( f_v \) becomes 0.08 and the apparent isotope effect disappears.

Although the information on the rotational distributions of ZnH and ZnD are not available yet, it is possible to estimate the upper limit of the rotational fraction, \( f_r \). This can be obtained by assuming that the rotational population increases in proportion to its degeneracy. The upper limits of \( f_r \) for ZnH and ZnD are 0.15 and 0.16, respectively. In this estimation, only the rotational levels below the dissociation limits were taken into account. Then, it can be concluded that more than 75% of the available energy is partitioned into the translational energy, almost into that of H or D atoms.
Finally, it should be noted that the population of ZnH(ZnD) via Zn(4^3P_J) can be ignored. This is because the efficiency for the intersystem crossing by H_2 is extremely low.\textsuperscript{23}

**DISCUSSION**

Table 1 gives the results of the prior and the phase-space calculations. In this calculation, only the populations of the rotational levels below the dissociation limits were summed. The available energy was set equal to the sum of the exothermicity and the thermal energy, (5/2)RT. The agreement between the experimental distributions and the statistical ones is poor. The lifetime of the intermediate complex must be too short to randomize the available energy. This is consistent with the results for the quenching of Zn(4^1P_J) by CH_4. The rotational distribution of ZnH produced from CH_4 is also much hotter than the statistical one.\textsuperscript{15}

The small partitioning of the available energy into the vibrational mode excludes the possibility of the collinear heavy-light-light geometry for the intermediate. In other words, the side-on attack of the H–H bond by Zn(4^1P_J) is indicated. This conclusion is consistent with the results of other excited metal–H_2 systems.\textsuperscript{4-8} It has been discussed that the production of group 2 and 12 metal hydrides, M–H, from these metal atoms in excited states and hydrogen molecules proceeds via bent insertive H–M–H intermediates; via 'B_2 or ^3B_2 state in C_{2v} symmetry and the 'A' or ^3A' state in C_3 symmetry. The rotational excitation of M–H results from an angular dependence of the interaction potential at the exit channel. Monotonous decrease in the vibrational population has also been observed in the quenching of Zn(4^3P_J), Hg(6^3P_J) and Mg(3^1P_J).\textsuperscript{5,8,24}

The quantum yield of ZnH for H_2 is much smaller than that for CH_4. In the Zn(4^1P_J) + CH_4 system, the absolute quantum yield for the production of ZnH must be less than unity. This is because three-body dissociation to produce Zn + H + CH_3 is energetically possible and the rotational distribution seems to extend over the rotational dissociation limit of ZnH, N = 34.\textsuperscript{15} The rotational distribution could be expressed by a Boltzmann distribution around 10^4 K. By extrapolating this distribution and assuming that the rotational levels over the dissociation limit predissociate, it is possible to estimate the ratio of the two-body and three-body dissociation processes to be 7:3. Then, the absolute yield for the production of ZnH for CH_4 is less than 0.7. The absolute yield for H_2, therefore, must be less than 0.35. In order to explain this small yield, it is necessary to assume that three-body dissociation processes to produce Zn + H + H is dominant. One of the most plausible processes is the rotational predissociation of ZnH. Similar processes have been postulated in the quenching of Zn(4^3P_J) by H_2O as well as that of Hg(6^3P_J) by H_2.\textsuperscript{14,25} Direct production of H_2(\Sigma_g^+) must be minor since this process is spin-forbidden and non-Franck-Condon. The presence of rotational predissociation processes again indicates that the intermediate is non-linear.
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