# Laserproduction of NaH crystalline particles

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# Laser-production of NaH crystalline particles

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Production of NaH crystalline particles of $\mu$m size is observed in sodium vapor mixed with $\sim 10$ Torr $H_2$. The particles are produced when $Na_2$ is excited to the $B\,^1\Pi_u$ state by a cw $Ar^+$ laser, and also when Na is excited by a cw dye laser tuned to the $D_1$ or $D_2$ line.

## I. INTRODUCTION

In 1975 Tam *et al.*[1] reported the phenomenon that, when cesium atoms in hydrogen gas are excited by a laser beam to the excited states such as $8D$ and $7P$, $\mu$m size crystalline particles of CsH are formed. It is now believed that these particles are formed by the condensation of CsH molecules which are produced by the chemical reactions as

$$Cs^* + H_2 \rightarrow CsH + H\,, \tag{1}$$

$$Cs + H + X \rightarrow CsH + X\,, \tag{2}$$

where X represents any atom or molecule in the ground electronic state. The produced particles are called "laser snow,"[2] because they are white crystals and fall down from the laser beam through gravity. Furthermore, the temperature of the falling particles is expected to be cold due to evaporation, when they are produced in a relatively high temperature.[3] Oscillating particle formation (frequency: 0.1–1 Hz) has also been observed in a mixture of Cs vapor and $D_2$ gas under a relatively strong excitation of Cs atoms.[4]

In this paper we report on the first observation of laser-production of NaH crystalline particles (laser snow) in sodium vapor mixed with hydrogen gas. It should be emphasized that we could observe the particle formation when the sodium molecules were excited by a visible $Ar^+$ laser ($\lambda$: 457.9–514.5 nm) to the $B\,^1\Pi_u$ state. This is apparently due to the condensation of NaH molecules produced by the reaction of the excited sodium molecules with the hydrogen molecules, and this kind of photochemical reaction in a mixture of alkali-metal vapor and hydrogen gas has not been reported yet. We could also observe the particle formation when we excited sodium atoms to the $3P$ states by a cw dye laser tuned to the $D_1$ and $D_2$ line, although these states do not have the energies required for the reaction corresponding to (1). We report also on the experimental evidence of the dissociation of the produced NaH dimers and particles by collisions with sodium atoms in the $3P$ states. Such dissociation by the alkali-metal atoms in the first-excited $P$ states does not occur for the other alkali-hydride laser snow observed so far.

## II. PARTICLE FORMATION BY THE EXCITATION OF $Na_2$

Figure 1(a) shows the simple experimental setup used to observe the NaH particle formation by an $Ar^+$ laser beam. In this experiment we did not select a particular line of the $Ar^+$ laser lines, so that five or six lines were simultaneously oscillating in the visible region between 457.9 and 514.5 nm. It is well known that almost all of these $Ar^+$ laser lines can excite $Na_2$ molecules from the ground electronic state $X\,^1\Sigma_g^+$ to the $B\,^1\Pi_u$ state.[5] The $Ar^+$ laser beam was focused by a lens (focal length: 20 cm) and applied to the glass cell containing Na vapor mixed with $H_2$ gas of 10 Torr and He gas of about 500 Torr, which was used as a buffer gas. We used the high pressure He buffer gas to make the movement of the produced particles slow enough to be able to observe individual visible-size particles, although the particle formation could be observed in a cell without the buffer gas. The cell used was cylindrical with a 4 cm i.d. and a 5 cm length, which was made of aluminosilicate (Corning 1720) glass. The cell was placed in a transparent glass oven which was carefully designed so that the convection within the cell was minimized. It is noted that the cell should be baked out at a temperature higher than 500 °C, in a vacuum, for about 24 hours before filling. When the baking was not sufficient, we could not observe the particle formation. This must be due to the presence of $Na_2O$ on the surface of the walls, which reacts quickly with $H_2$, resulting in a considerable decrease of $H_2$ pressure.

Figure 1(b) is a photograph showing the strong Mie scattering of the $Ar^+$ laser beam by the produced particles, which was taken about 5 sec after the irradiation, in the case that the temperature of the cell was 280 °C and the laser power was about 1 W. Within a few seconds after the laser irradiation, the particles grew; the largest particles being visible after settling down

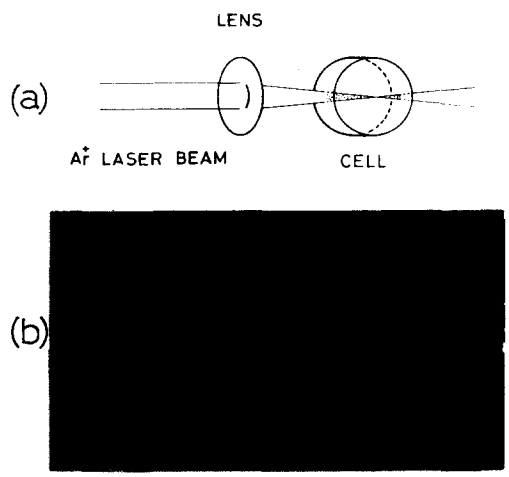


FIG. 1. (a) Experimental setup, and (b) a photograph showing the Mie scattering of the $Ar^+$ laser beam by the produced NaH particles.

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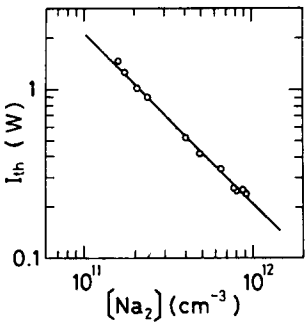


FIG. 2. Threshold $Ar^+$ laser power $I_{th}$ for particle formation as a function of $Na_2$ density $[Na_2]$.

from the laser beam through gravity with a velocity of about 1 mm/sec. By equating the force of gravity to the viscous retarding force of the He buffer gas, we could estimate the size of the largest particles to be about 1 $\mu$m, which is approximately the same as the laser-produced CsH particles observed by Tam *et al.*[1]

We measured the laser threshold power for the production of particles as the temperature of the cell was varied from about 240 °C–285 °C. Figure 2 shows the threshold power $I_{th}$ of the $Ar^+$ laser beam as a function of molecular sodium density $[Na_2]$, which was determined from the measured temperature. We see from Fig. 2 that the threshold condition for the NaH particle formation can be expressed as

$$I_{th}(T)[Na_2](T) = \text{const.} \tag{3}$$

When the saturation in absorption of the $Ar^+$ laser beam can be neglected, the density of sodium molecules in the $B\,^1\Pi_u$ state is proportional to the quantity $I_{th}[Na_2]$. Consequently, the threshold condition (3) shows the fact that when the density of sodium molecules in the $B\,^1\Pi_u$ state reaches a certain value, the density of the produced NaH molecules becomes its critical value $[NaH]_c$ for condensation.

The most probable chemical reaction to produce the NaH molecules is, in the present stage, considered to be

$$Na_2(B\,^1\Pi_u) + H_2 \rightarrow 2NaH\,, \tag{4}$$

which is energetically possible. The energy of the $B\,^1\Pi_u$ state at the bottom of the potential well is 1.82 eV,[6] and the dissociation energies of $Na_2$ and $H_2$ in the ground states are known to be $D(Na_2) = 0.73$ eV,[7] and $D(H_2) = 2.47$ eV.[8] While the dissociation energy of NaH, $D$(NaH) is not accurately known, it has been calculated to be 1.88 eV,[9] or 1.79 eV,[10] (the extrapolation of the measured ground state vibrational levels suggests 2.12 eV).[11] One may find that Reaction (4) is consistent with the experimentally obtained relation of $I_{th}(T)$ and $[Na_2](T)$, which is given by (3).

Another possible mechanism to produce NaH molecules is the reaction of sodium atoms in the highly excited states, which may be created indirectly from $Na_2(B\,^1\Pi_u)$ through the process: $Na_2(B\,^1\Pi_u) \rightarrow Na(3P) \rightarrow Na(nX)$. The excitation of sodium atoms to the $3P$ states is possible partially by the dissociation of $Na_2(B\,^1\Pi_u)$ and partially by the energy transfer collisions of these excited molecules with ground-state sodium atoms.[12] As described later, the energies of the $3P$ states are not enough to produce NaH by the reaction corresponding to (1). The excitation from the $3P$ states to some highly excited $S$ or $D$ states may occur by (a) collisions between $3P$-state atoms, and by (b) the laser excitation through the far wings of absorption lines broadened by He gas. We found, however, that both of the processes (a) and (b) were not dominant for the production of NaH in the present experiment. To check the process (a), we excited sodium atoms directly by a dye laser instead of the $Ar^+$ laser, and we found that even when the $D_1$ or $D_2$ fluorescence for the dye laser excitation is a few times stronger than that for the $Ar^+$ laser excitation, we could not observe the particle formation. As to the process (b), the 514.5 nm line of the $Ar^+$ laser is, for example, very close to the transition frequencies from the $3P$ states to the $6S$ state ($\Delta\nu \sim 15$ cm$^{-1}$). However, if we assume that the process (b) is dominant, the threshold laser power as a function of $Na_2$ density must be given by $I_{th}^2[Na_2] = \text{const}$, which disagrees with the experimental result given by Eq. (3). In this way we could ascertain that the $Na_2$ molecules in the $B\,^1\Pi_u$ state excited by the $Ar^+$ laser beam directly produce NaH through Reaction (4).

## III. PARTICLE FORMATION BY THE EXCITATION OF Na ATOMS

As described already, the alkali-hydride laser snow has been observed by exciting alkali-metal atoms such as Cs, Rb, and K in a hydrogen gas,[13] but there has been no report on the production of NaH particles by the excitation of Na atoms. To know whether or not similar particle formation takes place, we applied the cw dye laser beam tuned at the $D_1$ or $D_2$ line of sodium onto the same cell as described in II. In the case of the excitation of Na atoms, the expected chemical reactions with $H_2$ molecules are

$$Na^* + H_2 \rightarrow NaH + H\,, \tag{5}$$

$$Na^* + H_2 \rightarrow Na + 2H\,, \tag{6}$$

$$Na + H + He \rightarrow NaH + He. \tag{7}$$

Reactions (5) and (7) are the same types as (1) and (2). When we can neglect a small change in the kinetic energy of the system, we see, from the conservation of internal energies before and after the reactions, that the energy of Na*, i.e., $E$(Na*), required for Reactions (5) and (6) must satisfy, respectively, the following conditions:

$$E(Na^*) > D(H_2) - D(NaH)\,, \tag{8}$$

$$E(Na^*) > D(H_2)\,. \tag{9}$$

From Conditions (8) and (9) we see that the sodium atoms in the $3P$ states (energies ~2.1 eV) have not enough energy for Reactions (5) and (6). However, when the population of the $3P$-state atoms is large, the excitation to higher energy states becomes possible, as seen in the experiment by Allegrini *et al.*[14] who observed the fluorescence from the states $3D$, $5S$, $4D$, $6S$, and $5D$ for the $D$-line excitation of sodium atoms. They considered that the excitation to these states is due to the collisions between $3P$-state atoms, i.e.,

$$Na(3P) + Na(3P) \rightarrow Na(3S) + Na(nX) + \Delta E \ , \qquad (10)$$

although the energy defect $\Delta E$ is relatively large ($|\Delta E| > 600\ cm^{-1}$). To remove the difficulty of the large energy defect, Geltman[15] suggested another mechanism for this excitation, wherein he emphasized the importance of photoionization of the $3P$-state atoms. Here we will not discuss the excitation mechanism, but we stress only the experimental fact, shown by Allegrini *et al.*[14] that the $3P$-state sodium atoms produce the atoms in the states $3D$, $5S$, and $4D$, which satisfy Condition (8), and in the states $5S$ and $5D$, which satisfy Condition (9).

In the present experiment, the dye laser was tuned to the $D_1$ or $D_2$ line of sodium, and the spectral width of the laser light was about 10 GHz. As described already, the cell used contains He gas of about 500 Torr, which results in the pressure broadening of the $D$ lines of about 5 GHz,[16] so that almost all of the longitudinal modes of laser light can be considered to contribute to the excitation of sodium atoms. Similar to the experiment with an $Ar^+$ laser described in II, we have measured the threshold laser power $I_{th}$ for the formation of particles as a function of the temperature of the cell. Figure 3 shows $I_{th}$, when the laser was tuned at the $D_1$ line, against the sodium density [Na] calculated from the cell temperature. We can see in Fig. 3 that $I_{th}$ is approximately proportional to the inverse of [Na]; i.e., the threshold condition for the particle formation is given by

$$I_{th}[\mathrm{Na}] = \mathrm{const.} \qquad (11)$$

When the saturation of the transition from the $3S$ state to the $3P_{1/2}$ state can be neglected, $I_{th}$[Na] is proportional to the population of Na atoms in the $3P$ states (the $3P_{1/2}$ and $3P_{3/2}$ states are completely mixed by the collisions with He atoms). Consequently, Eq. (11) implies that the particle formation begins when the population in the $3P$ states reaches a certain value. Since the $3P$ states do not have the energies required for Reactions (5) and (6), the threshold condition must be rewritten as

$$[Na(nX)] \propto (I_{th}[\mathrm{Na}])^m = \mathrm{const} \ , \qquad (12)$$

where $Na(nX)$ is a Na atom in the highly excited state satisfying Conditions (8) or (9), and $m$ is an integer determined by the excitation mechanism to this state.

It is important to notice that the $3P$ states have energies higher than the dissociation energy $D$(NaH) of NaH (theoretical value: 1.88 eV,[9] or 1.79 eV,[10]) or comparable to $D$(NaH) (experimental value: 2.12 eV,[10]). Namely, the $3P$-state atoms may dissociate the NaH molecules, which are produced indirectly by these atoms through the excitation to higher energy states. This effect could be observed in the experiment where the $Ar^+$ laser beam and the dye laser beam were applied to the cell simultaneously. The power of the $Ar^+$ laser was set above the threshold value for the particle formation, while the power of the dye laser tuned at the $D_1$ line was set low enough not to produce the particles by itself. In this experimental arrangement, we could see that the particles produced by the $Ar^+$ laser beam disappeared entirely in the region where two laser beams overlapped, as sketched in Fig. 4. This phenomenon indicates clearly the fact that both NaH and larger $(NaH)_n$ particles are dissociated by the collisions with the Na atoms in the $3P$ states. In the cases of laser production of other alkali hydride molecules such as CsH, RbH, and KH, which have been observed so far, the energies of the first $P$ states of Cs, Rb, and K are lower than the dissociation energies of these molecules, so that the collisions with the atoms in the first $P$ states do not greatly affect the density of the produced alkali hydride molecules.

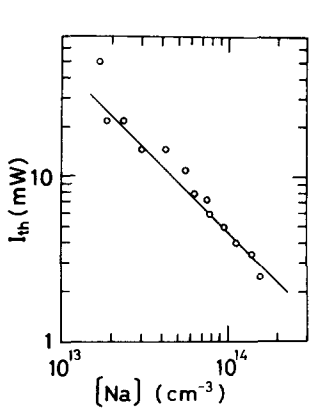


FIG. 3. Threshold power $I_{th}$ of the dye laser tuned at the $D_1$ line for particle formation as a function of Na density [Na].

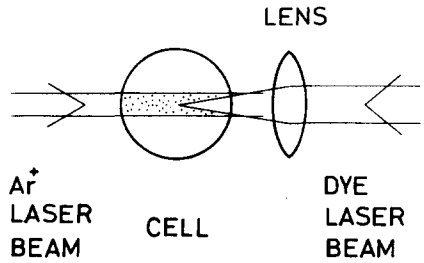


FIG. 4. Sketch showing the observed dissociation of NaH particles produced by $Ar^+$ laser beam in the region where the dye laser beam tuned at the $D_1$ line is applied.

## IV. CONCLUSION

In this paper, we have reported the first observation of NaH crystalline particles which are produced by the laser excitation of sodium atoms or molecules in a hydrogen gas. The size of the largest particles produced has been estimated from their falling velocity to be about 1 $\mu$m. We have observed also the dissociation of NaH and $(NaH)_n$ particles by the collisions with sodium atoms in the $3P$ states. The experimental results reported in this paper are with respect to the cell containing He gas of about 500 Torr in addition to Na vapor and $H_2$ gas of 10 Torr. Using the cell containing He gas of the same pressure, we could observe the particle formation even when the $H_2$ pressure was a few Torr. On the other hand, the particles were produced also in a cell without He gas when the $H_2$ gas was higher than 30 Torr. This dependence of He pressure on the $H_2$ pressure required for the particle formation must be due to the diffusion of the produced NaH molecules. Namely, in a high pressure buffer gas, the density of the produced NaH must be locally high within the laser beam, and the

condensation takes place even in a $H_2$ gas of low pressure.

A relatively large amount of sodium atoms are known to exist together with hydrogen gas in the upper atmosphere of the Earth and in the atmosphere of Jupiter (and, in particular, its satellite Io), where strong uv and visible radiation exists which is suitable to excite sodium atoms to the highly excited states. Consequently, in these atmospheres, the photochemical reactions reported in this paper can be considered to more or less take place.

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