

Study of Nascent NaH in Sodium-Hydrogen Mixture Using Resonant CARS and FWM Processes

R.R.B. Correia: S.L.S. Cunha: M. Motzkus G. Pichler[†] and P. Hering
Max-Planck Institut für Quantenoptik, W-8046 Garching, Germany

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The Coherent anti-Stokes Raman Spectroscopy (CARS) technique was applied to measure the O, Q, and S branches from the first, second and third overtones of the $X^1\Sigma^+$ ground state of NaH. Moreover, P and R doublets were also measured when the anti-Stokes signal was resonant with some lines of the electronic transition $A^1\Sigma^+ - X^1\Sigma^+$ of NaH. The high sensitivity resulting from pump laser resonances allowed us to study the $Na(nl) + H_2 \rightarrow NaH + H$ reaction dynamics.

I. Introduction

In the experiment reported here NaH was produced in a mixture of molecular hydrogen and sodium vapor through reactive collisions, when sodium was excited in the 3p, 5s, 4d atomic states respectively. The reaction of Na(3p) with the H_2 producing NaH is endothermic by 0.5 eV, but was nevertheless observed in our experiment as reported before by others workers^{1,2}. Some explanations for this reaction were proposed involving intermediate steps, as energy pooling producing highly excited sodium atoms². Other two possibilities could be the quenching of the excited sodium producing vibrationally excited molecules, which may collide once again with Na(3p), or the formation of an intermediate exciplex state followed by a two photon absorption.

With CARS technique (Coherent anti-Stokes Raman Spectroscopy) we observed O, Q and S lines of the first, second and third overtones ($\Delta v = 2, 3$ and 4) of the nascent NaH in its $X^1\Sigma^+$ ground electronic state, when the Stokes laser frequency was detuned by 2000 cm^{-1} up to 4500 cm^{-1} from the CARS pump laser frequency. These CARS overtone signals were strongly enhanced when the CARS pump laser frequency was tuned close to resonance with some lines of the electronic transition $X^1\Sigma^+ - A^1\Sigma^+$ in the NaH. We observed in addition on the same spectra, other lines that could not be assigned to CARS resonances but could be grouped as P and R doublets assigned to transitions between the first excited and the ground electronic states $A^1\Sigma^+ - X^1\Sigma^+$ ($v''=0, v'=8-13; J''=0-15, J'=J''\pm 1$) of NaH, excited in a resonant FWM (four wave mixing) process.

Due to the additional A-X electronic resonances

*Permanent address: Instituto de Física da Universidade Federal do Rio Grande do Sul, CxP. 15051, 91500 Porto Alegre, RS, Brazil

[†]Permanent address: Institute of Physics of the University, P.O. Box 304, YU-41001 Zagreb, Croatia.

with the pump laser, both signals becomes very large, increasing the sensitivity of the technique. From that property as well from its high temporal and spatial resolution, this new tool proved to be promising in the studies of the nascent NaH produced in this chemical reaction. This technique can help us to get some insight on the reaction dynamics, but one has to consider the difficulties for a quantitative analysis as a consequence of this resonant enhancement, which may be orders of magnitudes larger than the usual CARS signals, as well the effect of this resonance on the line profiles.

II. Experimental Setup

The experimental setup has been already described elsewhere³, but some modifications were introduced to observe the nascent NaH⁴. The lasers used for the CARS and FWM processes in our system were two excimer-pumped narrow band dye lasers. The CARS pump dye laser could be tuned in the blue spectral regions (440nm-450nm), corresponding to resonances of the first two vibrational bands of the electronic transition $A^1\Sigma^+ - X^1\Sigma^+$ of NaH. The Stokes laser was scanned in the green spectral region, allowing us to observe CARS spectra between 2000 and 4500 cm^{-1} and anti-Stokes signal in the near UV region. In addition to the filters used to separate the laser beams from the anti-Stokes signal, color filters were used to block the strong coherent emission from Na(4p-3s) transition when Na was excited with 2 photons (into 4d and 5s) due to a parametric process⁵.

The sodium vapor was produced in a heat-pipe oven using H_2 as buffer gas. For oven temperatures between 523 and 600 K, we observed optimal NaH signal at H_2 pressures between 50 and 100 mbar when sodium was excited into the 3p level.

To excite the Na atom we used either a flashlamp or an excimer-pumped dye laser. The flashlamp dye laser, with a pulse duration of $1.5\mu\text{s}$, yields large amounts

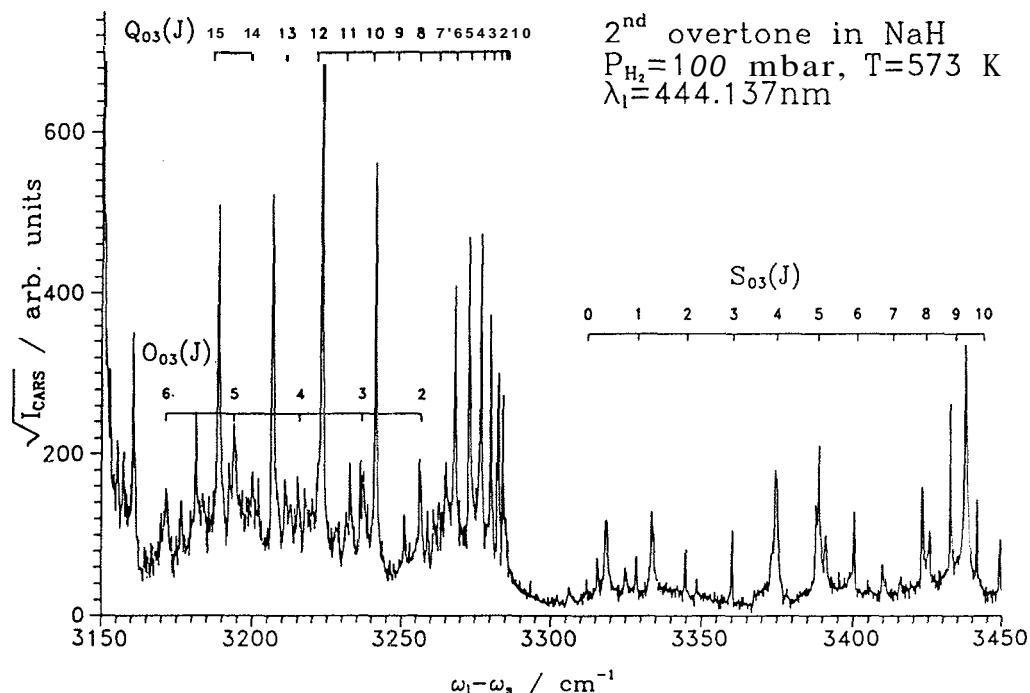


Figure 1.: Second NaH overtone $O_{03}(J)$, $Q_{03}(J)$ and $S_{03}(J)$ CARS lines. At higher J values, experimentally observed Q-lines are at larger frequency positions than theoretically predicted (shown by straight lines above the spectrum). The opposite is valid for S- lines.

of NaH due to the long integration time, The excimer-pumped dye laser, 10ns long, allows a much higher temporal resolution given by the pulse duration. The delay between the Na excitation and CARS lasers could be scanned in steps of 10ns, with jitter under 5ns, allowing to monitor the time evolution of the system. With this setup, we were also able to measure NaH excitation spectra, monitoring the intensity of the NaH overtones CARS lines, while scanning over the atomic Na lines.

III. Results and Discussion

Figure 1 shows the second overtone with O, Q and S branches of NaH, when Na is excited to the $3p$ state with the flashlamp-pumped dye laser at 589nm and the pump laser was tuned to 444.13nm. One can see that we were able to observe Q lines up to $J''=15$, where the line positions were calculated using recommended $X^1\Sigma^+$ Dunham coefficients⁶. We have also looked for transitions involving higher vibrational levels of the electronic ground state. Only a weak signal from the vibrational level $v''=1$ was observed at very short time delay and resonant conditions. This indicates that the nascent NaH is produced in this reaction, predominantly in the ground vibrational state.

The P and R doublets arise from FWM processes where the anti-Stokes wave is resonant with the $A^1\Sigma^+-X^1\Sigma^+$ electronic transition of NaH, involving high lying vibrational levels of the upper state ($v'=8-13$) and the first vibrational level $v''=0$ in the ground state. As for the overtone lines, J'' up to 15 were identified with

calculated values from recommended coefficients also available for this state $A^1\Sigma^+$ ⁶.

In the spectra of figure 2 the pump laser was tuned over some resonances of the $A^1\Sigma^+-X^1\Sigma^+$ electronic transition while the Stokes laser was scanned to get a CARS spectrum. In this spectrum the signal is represented against the $\omega_l - \omega_s$, where ω_l is the pump laser frequency and ω_s is the Stokes laser frequency. One has a CARS signal when this frequency difference corresponds to a Raman resonance in the molecule. These lines are stationary in the CARS representation. Otherwise one can see that the P and R doublets move in this representation, since $\omega_l - \omega_s$ doesn't match any Raman resonance while the anti-Stokes frequencies, $\omega_a = 2\omega_l - \omega_s$, are resonant with the electronic transition. When we detuned the pump laser as showed in figure 2, we observed a strong dependence of P and R doublets intensities, as of the CARS overtone lines intensities on the pump laser frequency, reflecting the influence of this extra electronic resonances. The assignment of the NaH lines was extremely difficult at the beginning, since we were not expecting such strong resonant behavior. Besides the amplification of lines, saturation effects were observed for overtone lines, so we had to attenuate the Stokes laser by a factor 50 in order to avoid these effects.

While tuning the pump laser over the A-X ($v''=0$, $v'=1-2$) electronic transitions, a similar behavior as showed in figure 3 was observed. This diagram was obtained measuring the area under the peaks of the

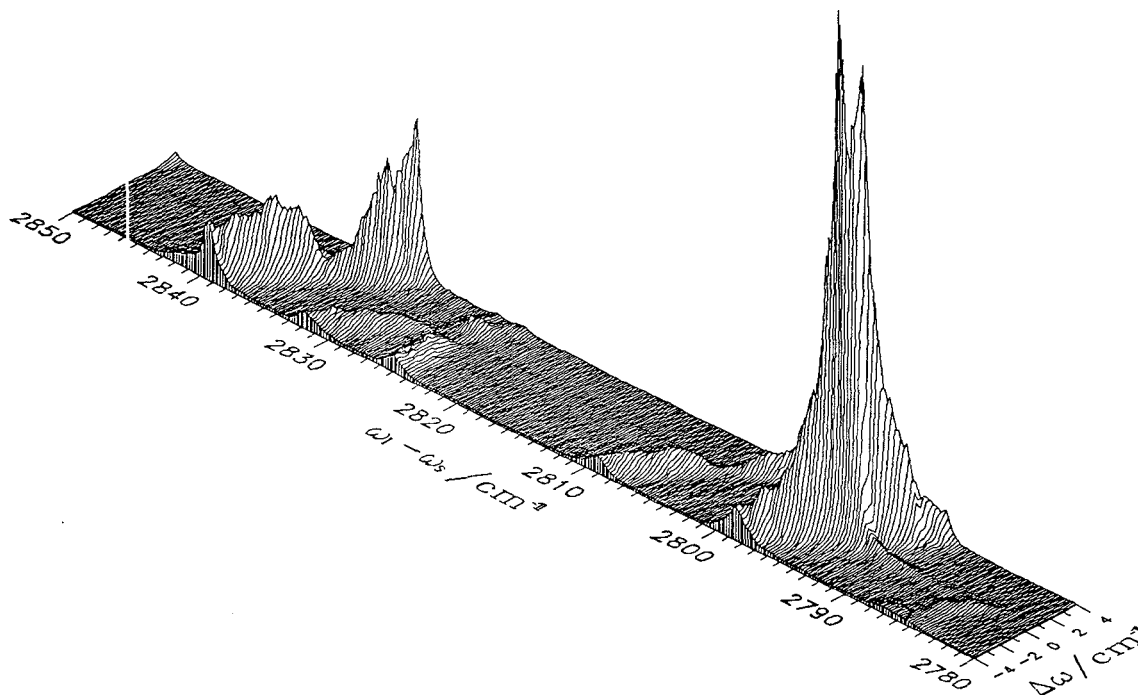


Figure 2.: Spectrit of the $P_5(9,0)$ and $R_5(9,0)$ lines of NaH, when the pump laser was tuned over the $P_5(1,0)$ electronic resonance.

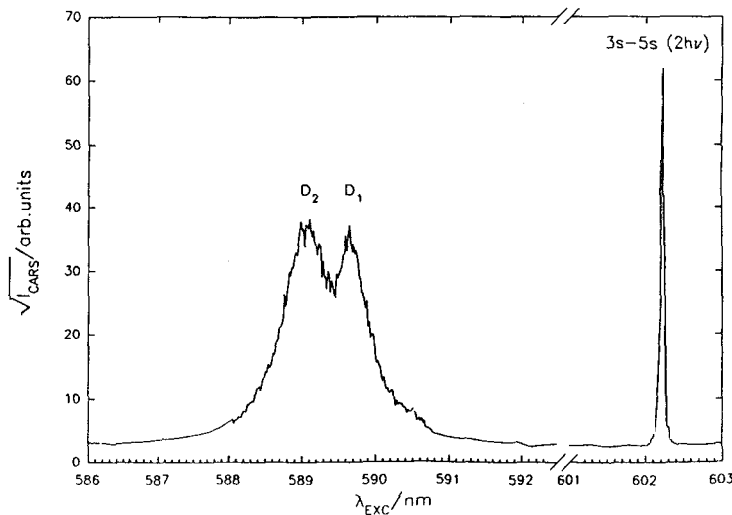
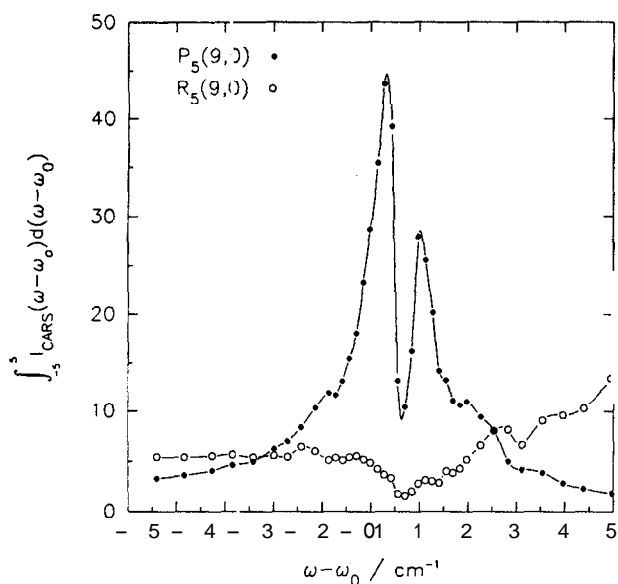


Figure 3.: Spectra obtained from figure 2 when the area under the $P_5(9,0)$ and $R_5(9,0)$ lines were measured in a 10cm^{-1} interval.

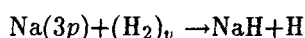
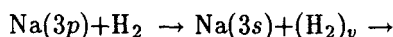
Figure 4.: Excitation spectrum measured at the NaH $Q_{03}(5)$ resonance CARS overtone line, while the Stokes laser was scanned over sodium D lines (left) and over 3s-5s two-photon transition (right). The temperature of the oven was 600 K, the pressure of hydrogen gas was 100 mbar and the time delay between the sodium excitation laser and the CARS lasers was 300ns.

$P_5(9,0)$ and $R_5(9,0)$ lines in Figure 2, in a 10cm^{-1} interval and plotted against the detuning frequency. The form of those lines shows that not only the signal may be strongly amplified due the resonance effect, but its maximum is also shifted relative to the resonance center.

Figure 4 shows an excitation spectrum done with the CARS frequency tuned at a $Q_{03}(1)$ line of NaH, while the excimer-pumped dye laser was scanned from 586 to 603 nm. For the 3s-5s 2-photon transition, we see no broadening at all. For the D_1 and D_2 lines of Na, the spectrum exhibits a strong broadening effect, probably caused by collisions and the high laser power.

In the case of the $3p$ state we would not expect any direct reactions with H_2 in the vibrational ground state, since it would be endothermic by 0.5 eV. However, this effect has already been predicted and observed before and the origin suggested to lie on the energy-pooling collisions between two Na($3p$) atoms², resulting in one ground state Na($3s$) and a highly excited Na(nl) in a Rydberg state. This excited sodium then reacts directly with H_2 producing NaH or decays to another excited state that does react⁷. This explanation seems reasonable since we know, from our spectrum, that NaH is produced by exciting directly Na($4d$) and Na($5s$) levels.

Otherwise, the fact that the quenching of Na($3p$) by H_2 at this pressures is very efficient, leads also to another possibility, already described for the similar system including cesium¹. This pathway is based on the fact that the hot vibrational $(H_2)_v$ resulting from the quenching collision with a Na($3p$), may collide with another Na($3p$) having enough energy to react and to produce NaH, as in the reaction below:



We have been doing efforts to determine the amount of Na($3p$) in our cell, relating it to the amount of sodium in Rydberg states and excited hydrogen molecules, in order to compare them with the observed amount of NaH. For a constant Na($3p$) concentration, one should expect, in the case of energy pooling, that the production rate of NaH will be constant. In the case of the reaction involving Na($3p$) and $(H_2)_v$, this rate will be proportional to the amount of $(H_2)_v$, which increases almost linearly with the time, due to the slow relaxation rates of $(H_2)_v$, $\tau_{relax} > 10\mu\text{s}$.

IV. Conclusion

CARS and FWM techniques were used to study the presence of NaH, produced in photochemical reactions between sodium in excited electronic states and H_2 , allowing us to observe the nascent vibrational and rotational distribution of this molecule. The detection of additional resonances in the pump laser has shown to

be a useful way to analyze the dynamics of those reactions with a higher sensitivity than the usual CARS nonresonant technique.

Acknowledgments

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