Towards redistribution laser cooling of molecular gases: Production of candidate molecules SrH by laser ablation.

P. Simon, P. Moroshkin, L. Weller, A Saß, and M. Weitz
Institute for Applied Physics, University of Bonn, Wegelerstr. 8, 53115 Bonn, Germany

ABSTRACT
Laser cooling by collisional redistribution of radiation has been successfully applied in the past for cooling dense atomic gases. Here we report on progress of work aiming at the demonstration of redistribution laser cooling in a molecular gas. The candidate molecule strontium monohydride is produced by laser ablation of strontium dihydride in a pressurized noble gas atmosphere. The composition of the ablation plasma plume is analyzed by measuring its emission spectrum. The dynamics of SrH molecular density following the ablation laser pulse is studied as a function of the buffer gas pressure and the laser intensity.

Keywords: Atomic collisions, redistribution of radiation, laser cooling, laser ablation, strontium monohydride

1. INTRODUCTION
Collisional redistribution laser cooling is a novel technique demonstrated for the first time by Vogl and Weitz in 2009. It is capable of laser cool "macroscopic" gas samples of alkali/noble buffer gas mixtures at typical buffer gas pressures of order of 100 bar. The cooling cycle proceeds in three steps: first, the atomic transition of the cooled species is shifted towards lower energies by a collision with a buffer-gas atom. At this moment, the atom absorbs a photon from a laser beam that is red-detuned from the undisturbed atomic transition. The two colliding atoms then spatially separate and the transition frequency returns to its undisturbed value. In the third step, the excited atom emits spontaneous radiation (fluorescence) at the undisturbed frequency and returns to the ground state. The energy difference between the absorbed and emitted photons is taken from the kinetic energy of the colliding atoms and the gas is thus cooled.

In the absence of inelastic collisions and saturation effects, the cooling power density is given by

$$P_{cool}(r, z) = I_{Las}(r, z) \alpha(\omega_{Las}) \frac{\omega_{Fluor} - \omega_{Las}}{\omega_{Las}}$$  (1)

Here, $I_{Las}(r, z)$ is the laser intensity, $\omega_{Las}$ - the laser frequency, $\alpha(\omega)$ - the absorption coefficient of the medium, and $\omega_{Fluor}$ - the mean frequency of the emitted spontaneous radiation, determined as a center of gravity of the collision-broadened fluorescence spectrum.

The typical energy that can be removed from the dense ensemble in one cooling cycle is of order of $k_B T$. Efficient cooling is thus possible at high initial temperature $T_0$ and requires a large rate of atomic collisions that can be achieved at a high buffer gas pressure $p$. It is also important that the red-detuned laser radiation is strongly absorbed by the gas, which requires a strong collision broadening of the atomic spectral line and a high number density of the absorbing atoms. The cooling effect was demonstrated in alkali-metal (Rb, K) vapors mixed with different noble gases (He, Ar) at the initial temperature of 500-700 K and the buffer gas pressure of 100-200 bar. Under these conditions, the sample is optically dense even at the used detunings of 10-20 nm with respect to the wavelength of the resonant transition of the alkali atom. The estimated cooling power reaches 100 mW corresponding to a cooling efficiency of $\approx 3\%$, being many orders of magnitude above the cooling efficiency in the Doppler cooling of dilute atomic gases. The cooling mechanism is rather general and can be applied to different species. In particular, we aim at a demonstration of the redistribution laser cooling effect in molecular/buffer gas mixtures.

As with other laser-cooling techniques the main difficulty in cooling molecules is due to the vibrational structure of molecular transitions that makes it difficult to obtain a closed transition for the excitation and reemission. For redistribution laser cooling, frequent collisions with buffer gas atoms are expected to cause
thermal equilibrium of the internal rotational and vibrational structure with the external degrees of freedom. Along with the large efficiency of laser redistribution cooling, with an energy removed per cooling cycle of order of $k_B T$, corresponding to $1/40$ eV at room temperature, the restriction to closed transitions is expected to be loosened. For Doppler laser cooling it was propose to use diatomic molecules with a diagonal Franck-Condon array. In this case, the molecule excited to the vibronic state with the vibrational quantum number $v$, can decay only to the lower electronic state with the same vibration number and one obtains a closed transition suitable for the laser cooling. Several compounds are known to possess this property, mostly monohydrides and monohalides of alkali-earth elements. Among them, $A^2\Pi \leftrightarrow X^2\Sigma$ band of SrH has a wavelength that can be reached by a high-power tunable Ti:sapphire laser. For this initial work we have chosen to start with such a molecule with an almost closed transition, aiming at a first demonstration of laser redistribution cooling with molecules.

Unfortunately, SrH, as well as other molecules of this group, is a chemically very active free radical and has to be produced directly in the cooling setup, in a dense buffer-gas atmosphere. It has been recently demonstrated that a very similar compound, CaH can be produced by laser ablation of a CaH$_2$ target in a cold He gas. Similar results were reported also on laser ablation of SrF$_2$ in He that yields SrF - another candidate molecule for redistribution laser cooling. We therefore have chosen laser ablation as the production method. However, obtaining a sufficient amount of SrH under high pressure of the buffer gas has proven difficult. It should be noted that in the existing studies laser ablation was successful at cryogenic temperatures and relatively low buffer-gas densities. Laser ablation of materials of this type under high buffer-gas pressure remains largely unexplored. The present contribution describes our approach and the current experimental status.

2. EXPERIMENT

2.1 Experimental setup

Our experimental setup is sketched in Fig. 1. We ablate SrH$_2$ by a frequency-doubled pulsed Nd:YAG laser ($\lambda = 532$ nm) with a pulse energy in the range of 2-10 mJ and a repetition rate of 10 Hz. The ablation target is prepared by pressing the SrH$_2$ powder by a hydraulic press developing a pressure of $\approx 400$ MPa. The target is installed at the bottom of a high-pressure sample cell filled with He or Ar buffer gas at a pressure of 0.5 - 10 bar. The cell is made of stainless steel with five sapphire windows. Four horizontal windows are used for the diagnostics and the top window for the ablation. The Nd:YAG laser beam is focused by a lens with a focal distance of 12 cm, mounted above the cell on a translation stage. We have obtained the most stable ablation yield with the lens positioned $\approx 10$ cm above the target surface. We estimate the beam cross section at the target surface as $S \approx 1$ mm$^2$. With more tight focusing, we observe that the laser beam creates a crater in the target surface on the time scale of several minutes. The ablation yield subsequently becomes strongly reduced.

In order to analyze the composition of the created ablation plasma, we collect the fluorescence emitted by the plume through one of the horizontal windows. The light is then coupled into a fiber and brought to a grating spectrometer with a resolution of 1 nm and covering a spectral range of 300-1000 nm.
Figure 2. Emission spectra of the ablation plasma plume in vacuum (a) and in the argon atmosphere (b). In (b), red line - \( p = 2 \) bar, blue line - \( p = 100 \) bar. Filled and empty triangles mark the transitions of Sr\(^+\) ions and Sr atoms, respectively, crosses mark the Ar lines.

We detect SrH molecules via their laser-induced fluorescence excited by a radiation of a cw Ti:sapphire laser pumped with a frequency-doubled diode-pumped solid state (DPSS) laser. The Ti:sapphire laser is tuned into resonance with the \( v = 0 \rightarrow v = 0 \) vibrational component of the \( X \, ^2\Sigma_{1/2} \rightarrow A \, ^2\Pi_{3/2} \) band at 733 nm. The laser beam passes through a pair of horizontal windows, 1-2 mm above the target surface. The fluorescence is collected at right angle with respect to the laser beam. The fluorescence is separated from the scattered laser beam light and ablation plume emission by means of a home-built monochromator utilizing a diffraction grating of 1200 grooves/mm and having a resolution of about 2 nm. The fluorescence signal is detected by a photomultiplier tube (PMT) and recorded by a digital oscilloscope. We detect the fluorescence at the \( v' = 0 \rightarrow v = 0 \) vibrational component of the \( A \, ^2\Pi_{1/2} \rightarrow X \, ^2\Sigma_{1/2} \) band at 745 nm. The \( A \, ^2\Pi_{1/2}(v' = 0) \) state lies 300 cm\(^{-1}\) below the laser-excited \( A \, ^2\Pi_{3/2}(v' = 0) \) state and is populated by atomic collisions.

2.2 Experimental results

Typical spectra of the emission produced by the ablation plume at different buffer gas (argon) pressures are shown in Fig. 2. The wavelengths of the observed lines and their assignments to the corresponding electronic transitions of Sr atoms and Sr\(^+\) ions are collected in Table 1 and Table 2 respectively. The near infrared part of the spectrum is dominated by Ar lines. In the violet part of spectrum we observe six strong lines of Sr\(^+\) ion. The spectral range of 450 - 700 nm contains mostly lines of the Sr atom. The \( H_\alpha \) line is visible at 656.3 nm. All other lines of atomic hydrogen overlap with much stronger lines of Sr and Sr\(^+\) and could not be observed. The atomic and ionic lines are strongly broadened by collisions. Increasing the Ar pressure leads to a stronger broadening and to the appearance of a continuous emission spectrum that extends over a wavelength range from 400 to 900 nm.

At high buffer gas pressure, the ablation plume becomes more compact since the ablation products experience more collisions with buffer gas atoms and thermalize at shorter distance from the surface. As a result, we obtain a higher density of the ablation products. It leads to a reabsorption of the emitted radiation by the atoms and ions in the plume. Those lines that terminate at the ground state therefore appear as dips in the emission spectrum. In Fig. 2 (b), one can see pronounced self-absorption dips at the wavelengths of the \( 5^2P_{3/2} - 5^2S_{1/2} \) and \( 5^2P_{1/2} - 5^2S_{1/2} \) lines of Sr\(^+\) at 407.8 and 421.5 nm, respectively and of the \( 5^1P_1 - 5^1S_0 \) transition of Sr at 460.7 nm.
Table 1. Electronic transitions of Sr atoms observed in the fluorescence emitted by the laser-ablation plume.

| transition | λ (nm) | transition | λ (nm) |
|------------|--------|------------|--------|
| 5s6f - 5s4d | 1F_3 - 1D_2 | 440.6 | 3D_1 - 3P_0 | 483.2 |
| 5s7s - 5s5p | 3S_1 - 3P_2 | 443.8 | 5s5d - 5s5p | 3D_2 - 3P_1 | 487.2 |
| 5s5p - 5s² | 1P_1 - 1S_0 | 460.7 | 3D_3 - 3P_2 | 496.2 |
| 5s5f - 5s4d | 1F_3 - 1D_2 | 467.8 | 1D_2 - 1P_1 | 767.3 |
| 5p² - 5s5p | 1P_2 - 1P_1 | 472.2 | 1P_1 - 1D_2 | 475.5 |
| 5s4f - 5s4d | 3F_4 - 3D_3 | 489.2 | 3D_2 - 3D_2 | 550.4 |
| 5s5f - 5s4d | 1F_3 - 1D_2 | 515.6 | 4d5p - 5s4d | 3D_1 - 3D_1 | 552.2 |
| 5s6p - 5s4d | 3P_1 - 3D_2 | 634.6 | 3D_2 - 3D_2 | 650.4 |
| 5s6f - 5s5p | 3S_1 - 3P_0 | 670.1 | 3F_2 - 3D_2 | 661.7 |
| 5s6s - 5s5p | 3S_1 - 3P_1 | 687.8 | 1D_2 - 1D_2 | 730.9 |
| 5s6f - 5s5p | 3S_1 - 3P_2 | 707.0 | 3F_2 - 1D_2 | 762.1 |

Table 2. Electronic transitions of Sr⁺ ions observed in the fluorescence emitted by the laser-ablation plume.

| transition | λ (nm) |
|------------|--------|
| 4p^65d - 4p^65p | 2D_5/2 - 2P_3/2 | 338.1 |
| 4p^65p - 4p^65s | 2P_1/2 - 2S_1/2 | 407.8 |
| 4p^66s - 4p^65s | 2S_1/2 - 2P_1/2 | 416.2 |
The observed fluorescence spectra demonstrate high densities of Sr atoms and Sr$^+$ ions produced by laser decomposition of SrH$_2$. However, no spectral features of SrH or SrH$_2$ molecules could be detected in the plasma plume spectra. These observations suggest that the laser ablation leads to a complete decomposition of SrH$_2$ molecules and to the strong ionization of the dissociation products. In order to search for the SrH molecules in the ablation plume at larger delay-times with respect to the laser pulse, we have excited the gas with a cw Ti:sapphire laser tuned in resonance with the $X^2\Sigma_{1/2}(v = 0) \rightarrow A^2\Pi_{3/2}(v' = 0)$ band at 733 nm. To avoid a strong background from scattered incident laser radiation, we monitor the fluorescence emitted by the $A^2\Pi_{1/2}(v' = 0)$ state that is located energetically below the $A^2\Pi_{3/2}(v' = 0)$ state and is populated by collisions with buffer gas atoms.

No SrH fluorescence could so far be detected in Ar buffer gas. However, we have observed a strong laser-induced fluorescence signal following the ablation of SrH$_2$ target in He atmosphere. A typical time-resolved fluorescence signal is shown in Fig. 3. The broadband emission of the ablation plasma plume is produced within a time interval of 200 ns immediately after the ablation laser pulse. It has been measured separately and then subtracted from the fluorescence signal. The radiative life time of the $A^2\Pi_{1/2}$ state of SrH, as measured by Berg et al., is 34 ns and that of $A^2\Pi_{3/2}$ is even shorter. The observed rise and decay of the SrH fluorescence excited by the resonant cw laser thus reflect the dynamics of the number density of the ground state SrH molecules. The signal rises after the ablation pulse, reaches a maximum at a delay time of $\approx 1 \mu$s and then decays exponentially with a decay-time of 8.6 $\mu$s.

The absorption spectrum of the $X^2\Sigma_{1/2}(v = 0) \rightarrow A^2\Pi_{3/2}(v' = 0)$ band of SrH was measured by scanning the excitation laser in the vicinity of $\lambda_{exc} = 733$ nm and measuring the fluorescence yield at $\lambda_{fluor} = 748$ nm, as a function of $\lambda_{exc}$. At low buffer gas pressures the rotational structure could be resolved, as shown in Fig. 4(a). One can see four resolved spectral components of the Q-branch, each of them overlapping with a much weaker line from the P-branch. The experimental spectrum is fitted with a sum of 8 Lorentzian curves having the same spectral width and centered at the positions of the rovibronic lines accordingly to the data of. The individual contributions of 8 lines are also shown by dashed lines. The lines are labeled by the total angular momentum quantum numbers $J$ of the corresponding lower states. This fit allows us to determine the spectral widths of the molecular lines broadened by collisions with the buffer gas atoms. At $p = 2$ bar, the FWHM spectral width of each line is $24.7 \pm 0.7$ GHz, which is much larger than the Doppler width at room temperature.

A typical excitation spectrum at a buffer gas pressure of 10 bar is shown in Fig. 4(b). At high pressure, the line broadening increases and the rotational structure can not be resolved any more. The whole band has a FWHM spectral width of $\approx 1$ nm and has broad spectral wings.

### 3. DISCUSSION

Our measurements demonstrate the feasibility of the production of SrH molecules by laser ablation of SrH$_2$ in a helium buffer gas atmosphere. The dominant species in the ablation plume are Sr atoms and Sr$^+$ ions.
During the laser pulse their number density reaches very high values, as is evidenced by the reabsorption of their fluorescence. On the other hand, SrH molecules could be detected in relatively smaller amounts and their observed lifetime after the ablation pulse is in the microseconds range. Surprisingly, no SrH spectral lines could so far be observed in argon buffer gas. A possible explanation for this would be that collisions with Ar atoms or some other ablation products effectively quench the excited states of SrH.

The measurements of the excitation spectrum of the $X^2\Sigma_{1/2}(v = 0) \rightarrow A^2\Pi_{3/2}(v' = 0)$ band provide information about the collision line broadening that is very important for the planned molecular redistribution cooling experiment. At buffer gas pressures above 10 bar, the collision-broadened rovibronic lines overlap strongly and form a continuous absorption spectrum. The $X^2\Sigma_{1/2}(v = 0) \rightarrow A^2\Pi_{3/2}(v' = 0)$ band itself is not suitable for the redistribution cooling experiment because the laser-excited molecules in the $A^2\Pi_{3/2}(v' = 0)$ state undergo radiationless transitions towards the lower lying $A^2\Pi_{1/2}(v' = 0)$ state. The energy difference of $\approx 300 \text{ cm}^{-1}$ is transferred into the kinetic energy and will lead to heating of the gas. On the other hand, redistribution laser cooling should be possible at the $X^2\Sigma_{1/2}(v = 0) \rightarrow A^2\Pi_{1/2}(v' = 0)$ band that is centered around 748 nm, which is expected to have a similar absorption spectrum.

The yield of SrH molecules achieved in the present experiment is relatively low compared to typical atomic densities in the so far carried out redistribution cooling experiments. In fact, we could so far not observe a measurable attenuation of the resonant laser beam crossing the sample cell. We expect that the yield can be substantially increased by increasing the laser power with a corresponding increase of the laser beam diameter at the target surface in order to keep the laser intensity fixed. We have obtained the best results with the laser fluences of order of $0.5 \text{ J/cm}^2$.

Another important observation is that of a decay of the molecular number density on the time-scale of 10 $\mu$s. Although the diffusion coefficient for SrH in He is not known, it is highly unlikely that a molecule can leave the observation volume and reach the cell wall in such a short time. Other loss mechanisms may include a chemical reaction in collisions with Sr or H atoms, the formation of clusters or condensation. An increase of the He pressure is expected to slow down the diffusion of SrH molecules. On the other hand, it will also make thermalization of the ablated species faster and confine the ablation plume close to the target surface. This in turn may lead to condensation of the ablated molecules into clusters or on the target surface. A similar behavior of laser-ablated Au and Li atoms in He buffer gas was reported by Sushkov and Budker. At low He densities they observed a diffusion-controlled dynamics of the atomic density with a typical decay time of order of several milliseconds. However, at densities above $10^{18} \text{ cm}^{-3}$, an additional loss mechanism starts to dominate that leads to a decrease of the decay time and of the ablation yield with increasing buffer gas density. The present work explored the range of He densities of $10^{19} - 10^{21} \text{ cm}^{-3}$. The observed yield and the short decay time are in
qualitative agreement with the results of.

4. SUMMARY
To conclude, we report on a study of the production of SrH molecules in noble buffer gas conditions at high pressures for redistribution laser cooling. The molecular sample was produced by laser ablation in a buffer gas cell. We investigate the spectral broadening of the $X \ ^2\Sigma_{1/2}(v = 0) \rightarrow A \ ^2\Pi_{3/2}(v' = 0)$ band of SrH by atomic collisions and the dynamics of the molecular density following the ablation laser pulse. For the future, we plan to carry out laser redistribution cooling of SrH molecules under high pressure noble buffer gas conditions.

ACKNOWLEDGMENTS
This work was supported by the Deutsche Forschungsgemeinschaft, grant No: We 1748-15.

REFERENCES
1. Vogl, U. and Weitz, M., “Laser cooling by collisional redistribution of radiation,” Nature 461, 70–73 (2009).
2. Vogl, U., Saß, A., Haßelmann, S., and Weitz, M., “Collisional redistribution laser cooling of a high-pressure atomic gas,” J. Mod. Optics 58(15), 1300–1309 (2011).
3. Saß, A., Vogl, U., and Weitz, M., “Laser cooling of potassium-argon gas mixture using collisional redistribution of radiation,” Appl. Phys. B 102, 503–507 (2011).
4. Vogl, U., Saß, A., and Weitz, M., “Laser cooling of dense rubidium-noble gas mixtures via collisional redistribution of radiation,” Proc. SPIE 8275, 827508 (2012).
5. Shuman, E. S., Barry, J. F., and DeMille, D., “Laser cooling of a diatomic molecule,” Nature 467, 820–823 (2010).
6. Di Rosa, M. D., “Laser cooling molecules,” Eur. Phys. J. D 31, 395–402 (2004).
7. Weinstein, J. D., de Carvalho, R., Guillet, T., Friedrich, B., and Doyle, J. M., “Magnetic trapping of calcium monohydride molecules at millikelvin temperatures,” Nature 395, 148–150 (1998).
8. de Carvalho, R., Doyle, J. M., Friedrich, B., Guillet, T., Kim, J., Patterson, D., and Weinstein, J. D., “Buffer-gas loaded magnetic traps for atoms and molecules: A primer,” Eur. Phys. J. D 7, 289–309 (1999).
9. Lu, H. I., Rasmussen, J., Wright, M. J., Patterson, D., and Doyle, J. M., “A cold and slow molecular beam,” Phys. Chem. Chem. Phys. 13, 18986–18990 (2011).
10. Barry, J. F., Shuman, E. S., and DeMille, D., “A bright, slow cryogenic molecular beam source for free radicals,” Phys. Chem. Chem. Phys. 13, 18936–18947 (2011).
11. Berg, L. E., Ekvall, K., Hishikawa, A., Kelly, S., and McGuinness, C., “Laser spectroscopy of SrH. Time-resolved measurements of the $A^2\Pi$ state,” Chem. Phys. Lett. 255, 419–424 (1996).
12. Watson, W. W. and Fredrickson, W. F., “The spectrum of strontium hydride,” Phys. Rev. 39, 765–777 (1932).
13. Appelblad, O., Klyming, L., and Johns, J. W. C., “Fourier transform spectroscopy of SrH: The $A - X$ and $B - X$ band systems,” Phys. Scripta 33, 415–419 (1986).
14. Sushkov, A. O. and Bulker, D., “Production of long-lived atomic vapor inside high-density buffer gas,” Phys. Rev. A 77, 042707 (2008).