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Studies of Laser Induced Cesium and Rubidium Hydride Formation in Vapor Cells and Their Application for Isotope Separation
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Brief overview and background

Basic concept

Hydride formation in the cell volume

Hydride formation on the cell window

Experiments and results

Model and calculations

Hyperfine structure of D-lines of Cs isotopes

Determination of abundance

Conclusion
Background

Industrially realized non-laser techniques:
Gas diffusion; Gas centrifugation

Industrially realized laser techniques:
Selective ionization

Published possible laser techniques:
Selective high-level excitation
The basic concept is:

*Alkali atoms do not react with hydrogen molecules in their ground states.*

However, when excited, they do.

*Excitation may be realized isotope-selectively by narrow-line laser radiation*

We use the lowest excited state of Cs and Rb
As distinct from highly excited Cs atoms, the energy of those excited to the D-level is insufficient to form a hydride molecule in collision with a hydrogen molecule.

However, the reaction may proceed in two steps, as was obtained earlier in sodium vapor mixed with hydrogen.
The first step - quenching

The second step – molecule formation

Excited and not cesium

Excited and not hydrogen

CsH and H
The reaction may also proceed on the cell wall, when an atom (rubidium in our experiments) being excited by laser radiation collides with the cell wall.
In experiments with cesium vapor we exploited the group of hyperfine transitions \( F=4 \rightarrow F'=3;4;5 \) of D\(_2\) line of Cs atom. Scanning (fast or slow) the diode laser radiation through this group we measured the absorption in and fluorescence from the vapor versus the laser intensity.
We used “pure” cesium cells and those filled with 20 Torr Hydrogen.

The fast and slow scan regimes determine the time of interaction of cesium atoms with laser radiation, which determines the probabilities of laser induced processes, such as saturation, optical pumping, etc.; this time is essentially different for cases of absence and presence of hydrogen.

We have the following relevant time scales: time of flight of atoms through the beam and time of scan, within which the radiation is in resonance with the transitions above; these times determine the time of interaction.

The physics is as follows
When the scan is fast, the time of interaction between Cs atoms and laser radiation equals nearly the time of scanning $12 \mu$s, both with and without hydrogen.

When the scan is slow, this time equals nearly the time of flight of atoms through the laser beam $15 \mu$s in case of pure vapor and $30 \text{ ms}$ in case of presence of hydrogen:

The cause: density of hydrogen in our experiments exceeds by 7 orders of magnitude that of cesium: the number density of cesium vapor was $2.7 \cdot 10^{10} \text{ cm}^{-3}$ (room temperature); the intensity varied in the range $1.5 \cdot 10^{-4}$ to 40 mW/cm$^2$. 
A fragment of experimental setup for cesium measurements
The diagram of the Cs setup
Results of absorption (transmission) measurements
What is observed

In the absence of hydrogen absorption remains unchanged going to saturation for intensities higher than 1 mW/cm²

In the presence of hydrogen absorption drops essentially with the increase of intensity

Fast and slow scan cases do not practically differ in the absence of H₂, but exhibit significant difference in the presence of that

We explain this by the decrease of the number density of Cs atoms because of formation of cesium hydride molecules
Results of the fluorescence measurements

Fluorescence (a.u.) vs. Laser Intensity (mW/cm$^2$) for different transitions:
- $\nu_4$ Cs slow
- $\nu_4$ Cs fast
- $\nu_4$ Cs+H$_2$ slow
- $\nu_4$ Cs+H$_2$ fast
What is observed

*In the absence of hydrogen fluorescence rises up to highest intensities 40 mW/cm²*

*In the presence of hydrogen fluorescence drops by several orders of magnitude with the increase of intensity*

Fast and slow scan cases do not practically differ in the absence of H₂, but exhibit significant difference in the presence of that

*We explain this again by the decrease of the number density of excited Cs atoms because of formation of cesium hydride molecules and the optical pumping*
In experiments with rubidium vapor we exploited hyperfine transitions of the $D_1$ and/or $D_2$ lines of the Rb atom. Here is the relevant energy level diagram.
A fragment of experimental setup for rubidium measurements
Simplified diagram of the Rb setup

- Rb cell in the oven
- resonant laser beam
- window
- frequency control
- side arm
Three types of rubidium vapor cells were used.

The first type were the cells purified up to $10^{-6}$ T vacuum and containing only rubidium vapor.

The second type were the rubidium vapor cells purified in the same way as the first one, but filled with hydrogen.

The third type cells were purified to the $10^{-3}$ T vacuum without hydrogen.

The cells of all three types were exposed to the diode laser radiation from 30 min to 2.5 hours. The radiation in different experiments was either tuned to a specific D$_2$ hyperfine transition of a specific rubidium isotope or scanned through the entire spectrum of all hyperfine transitions of D$_2$ line (in this case the deposition if any contained both isotopes).

The windows of the cells of all types were made of either glass or sapphire. Two or more cells of each type were used. The temperature of the cells varied in the range 190-210°C in the side arm and 220-240°C in the cell body. This temperature range corresponds to the number density of rubidium atoms on the order of $10^{14}$ cm$^{-3}$. 
What is observed

The first type cells:

Strong blue emission in the direction opposite to that of laser radiation. This emission was observed as a spot inside the red ring.

No deposition on both cell windows and side surface.

The second type cells:

No backward blue scattering.

A deposition on both the sapphire windows and the glass side surface (cylindrical) when irradiated sufficiently long.

The third type cells:

Bright blue scattering.

A deposition.
Example:

10^{-3} \text{ vacuum, no hydrogen, } 240^\circ \text{C, half-hour irradiation, } F_g=1 \cap F_e=0; 1; 2 \text{ transitions of the } ^{87}\text{Rb.}
Analysis allow us to conclude that the deposited spot consists of mainly the rubidium hydride (along with other hydrogen containing compounds) which is formed in reactions between the laser excited rubidium atoms and the hydrogen (or water) molecules adsorbed on the inner surface of the cell.

The blue backward scattering is caused by the energy pooling processes and is suppressed by the presence of hydrogen in the cell volume.
Model and calculations

\[ \dot{n}_0 = - \sum_{i=1,2,3} w_i (n_0 - n_i) + \sum_{i=1,2,3} \gamma_i n_i + k_1 m \sum_{i=1,2,3} n_i - \lambda_a (n_0 - n) \]

\[ \dot{n}_i = w_i (n_0 - n_i) - \gamma_i' n_i - k_1 m n_i - k_2 m^* n_i \]

\[ \dot{m}^* = (k_1 m - k_2 m^*) \sum_{i=1,2,3} n_i - \lambda_m m^* \]

\[ \dot{m} = -k_1 m \sum_{i=1,2,3} n_i \]
Computations with the model described above were made by assuming $m=\text{const}$, since the number density of hydrogen molecules exceeds by many orders of magnitude that of cesium atoms and the excited hydrogen molecules. We computed from these equations the integral fluorescence as a function of the laser intensity.

In case of pure atomic vapor we have $m=0$, $k_{1,2}=0$, and the collisional contribution into the overall linewidth is negligible. The presence of hydrogen increases the overall linewidth and reduces the leaving rates.
Results of computations in these conditions:

*solid lines – theory, points - experiment*

\[
\kappa_{\text{eff}} = (1 \pm 0.3) \cdot 10^{-10} \text{ cm}^3\text{s}^{-1}
\]
For future application of the presented results we calculated the energy levels of all Cs isotopes (since the data available in literature have discrepancies).

The diagram of energy levels and transition strengths for D\textsubscript{1} line hyperfine transitions of three of these isotopes – 133, 135, 137, are presented below.
Note finally that for the determination of abundances of isotopes (Rb) and, thus, the enrichment degree, we elaborated and employ mainly two techniques.

The first: selective reflection from the deposited layer on the cell window with measuring the peaks caused by either isotope.

The second: recording fluorescence from the close-to-window volume of the cell in conditions when a second, fixed-frequency strong laser destroys the deposited layer.

Preliminary results for Rb: abundance of $^{85}$Rb may be raised up to 6 times.
Selective reflection technique for determination of isotopic abundance

$^{85}\text{Rb}/^{87}\text{Rb} = 72/28$

$^{85}\text{Rb}/^{87}\text{Rb} = 88.5/11.5$

$98.4/1.6$
Conclusion

Formation of cesium hydride takes place at illumination of a room-temperature mixture of Cs vapor with hydrogen by a laser radiation tuned to the resonance $D_2$ line of atomic Cs. The rate constant of a two-step reaction is evaluated by comparing the experimental results for the laser-intensity dependence of the integral fluorescence with those of calculations based on rate-equation model.

Both the (extremely simple) experimental technique and the model may be used for evaluation of rate constants of chemical reactions between different interacting components.

So, if selective excitation condition is satisfied, the photochemical reactions may be directly used for the highly selective extraction of chosen alkali isotope from the mixture.

In heated rubidium vapor cells a solid deposition is observed on the inner surface of the cell under laser irradiation exciting rubidium atoms. This may also be used for isotope separation.
Thank you very much for attention