Particle Formation by Resonant Laser Light in Alkali-Metal Vapor*

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Resonant laser light causes micron-sized particles to form in cesium vapor when a small amount of hydrogen gas is present in the vapor. The particles are identified as cesium-hydride crystals. This is the first observation of light-induced particle formation in metal vapors. The phenomenon has relevance to lasers and nonlinear optical devices based on dense alkali vapors, and it may also be of interest for laser isotope-separation schemes.

During the course of some recent optical-pumping experiments with dense, spin-polarized alkali vapors,[1] we noticed that a resonant laser beam would often cause small particles to appear. The particles caused intense Mie scattering of the laser light, and they could be recognized as individual specks with a strong lens (see Fig. 1). Tyndall first reported light-induced particle formation in "nitrite of butyl" in 1869, and numerous observations of light-induced particle formation have been reported since then.[2] However, ours seems to be the first observation of light-induced particle formation in metal vapors. These particles were a serious impediment to our optical-pumping experiments. They are also an important factor to consider in other situations where high-density alkali vapors are exposed to intense light (e.g., excimer lasers,[3] nonlinear frequency converters[4]), and the phenomenon may be of interest for the isotope separation of alkalis or of hydrogen.

We have observed the phenomenon of particle formation under resonant laser excitation for various alkali metals or their mixtures. For example, we have observed that a cell containing Cs and Na (in $\sim 10^4$:1 ratio in the vapor) with a few amagats of He and a trace amount of H_2 ($\sim 10^{-1}$ Torr) forms particles when a focused cw dye laser beam at 5890 Å is incident on it. However, in this paper, we shall mainly discuss the phenomenon observed for Cs mixed with either of the following "buffer" gases: (1) 1 amagat or more of He (or other noble gases) contaminated with 0.01% or more of H_2; (2) 50 Torr or more of pure H_2. The cells used for the observations were constructed from 21-mm-i.d. aluminosilicate glass, and they were baked for 12 h at 650°C in a vacuum of 10^{-6} Torr before filling. The "buffer" gas causes sufficient broadening of the 4555-4593-Å second resonance doublet of cesium that the cesium atoms can be excited into the $7P$ state by either the 4545 or 4579 Å lines of an Ar^+ laser (Spectra Physics Model No. 165-03). These lines, which we whall refer to hereafter as resonant laser lines, cause visible particles to form at temperatures ranging from 250 to 400°C, with a formation time of less than a second. The laser power is ~200 mW and focusing of the laser beam is usually not necessary. When there is no convection current in the cell, the particles formed by a nonfocused laser beam are observed to fall with speeds ~1 mm/sec. For a focused beam, the particles are sometimes trapped in the laser beam. Off-resonant Ar^+ laser lines (e.g., 4880 Å) do not stimulate the formation of particles although the off-resonant lines can be used to observe particles which have been formed by one of the resonant laser lines. The particles vanish within a few minutes when off-resonant light is used for observation.

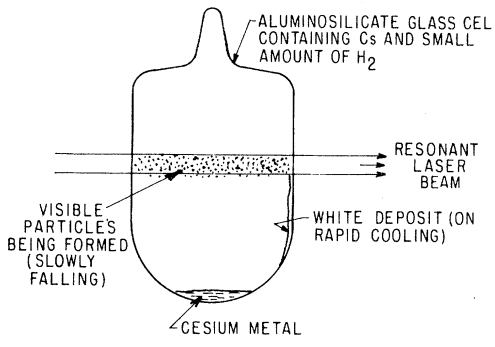

FIG. 1. Experimental arrangement. A transparent oven is not shown. The Mie scattering and fluorescence are viewed at right angles to the laser beam.

We considered and eliminated by experiment various mechanisms (e.g., diffusion cloud-chamber condensation,[5] cataphoresis[6]) whereby droplets of liquid cesium might possibly be formed by a light beam. We constructed cells with internal electrodes and we used methods similar to those

of the Millikan oil-drop experiment[7] to determine that the larger particles have sizes on the order of 10^{-4} cm and carry positive charges on the order of 10^4 electron charges.

The following points concerning the phenomenon are also noticed: (a) An aluminosilicate glass cell that has been baked at 500°C in a vacuum of 10^{-6} Torr before filling with Cs and a few amagats of pure He usually forms particles with resonant laser excitation, but a cell baked at 650°C and similarly filled does not. Apparently, water contaminant is not easily baked out at 500°C, and any residual traces of water in a cell would react with Cs to release free H_2. (b) If a sufficient density of N_2 (above ~100 Torr) is also present besides the He and H_2, then no particles can be formed. (c) If a sufficient amount of O_2 is introduced into a cell besides Cs, He, and H_2 on filling, so that all the H_2 would ultimately be gettered[8] as CsOH, then no particles can be formed. In other words, oxygen-rich cells do not form particles under resonant laser-light excitation, but hydrogen-rich cells do form particles. (d) Borosilicate Pyrex cells (filled similarly to the aluminosilicate cells normally used) form particles much less readily: Apparently, Na_2O is leached out of the borosilicate glass and it getters H_2; the sodium D lines can be clearly observed in Pyrex cells whenever Cs is excited by the laser, but the D lines are weak or unobservable in aluminosilicate cells.

The particles are identified as cesium-hydride condensates for the following reasons: (1) The presence of gaseous hydrogen is necessary for particle formation, and gettering it out results in no particle formation. (2) If the heaters for the cell oven are switched off so that a cell which was originally filled with 3 amagats of H_2 gradually cools down from 300°C, a white deposit forms on the glass wall in a vertical line just below the point of exit of the (focused) laser beam (see Fig. 1). (3) If a cell containing 0.1 amagat of hydrogen is excited with the 4579-Å line of the Ar^+ laser, one can see a progression of doublet fluorescent lines which we have identified[9] as P and R emission lines from the $v'=19$, $J'=10$ level of the CsH $A^1\Sigma^+$ state, which has been resonantly excited by the 4579-Å laser light from the $v''=0$, $J''=9$ level of the CsH $X^1\Sigma^+$ ground state. This is the first observation of emission lines from CsH molecules and details will be presented elsewhere.[10] The CsH fluorescent intensity is found to be roughly proportional to the $\frac{3}{2}$ power of the laser intensity (see Fig. 2). This implies that the

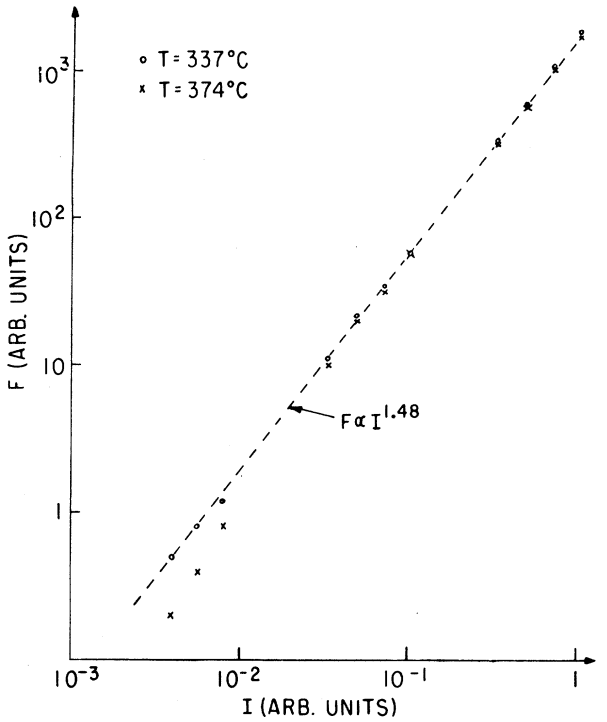

FIG. 2. Dependence of the intensity, F, of a CsH fluorescence line (4991 Å) on the incident 4579-Å laser intensity, I, for Cs with 50 Torr H_2.

CsH concentration in the vapor is proportional to the square root of the laser intensity. This $\frac{3}{2}$-power law is most simply explained as follows: The CsH molecules are formed by the resonant laser light at a rate proportional to the laser intensity and are destroyed mainly by collisions with other CsH molecules. Such collisions lead to $(CsH)_2$ dimers, which would polymerize further to form crystals of CsH.

The equilibrium partial pressures p of H_2, Cs, and CsH above a hydrogen-saturated solution of cesium in equilibrium with CsH crystals are shown in Fig. 3. The pressure of H_2 was computed from thermodynamic data,[11] and the vapor pressure of Cs was approximately by that of the pure metal because of the low solubility of hydrogen in cesium. The CsH partial pressure p(CsH) was calculated from the vapor-phase equilibrium equation

$$p^2(\mathrm{CsH}) = p^2(\mathrm{Cs})p(\mathrm{H_2})K.$$

The temperature-dependent equilibrium constant K was calculated[12] from the molecular dissociation energies, D [to which K is very sensitive; according to Gaydon,[9] $D(\mathrm{CsH}) = 1.8 \pm 0.3$ eV], and

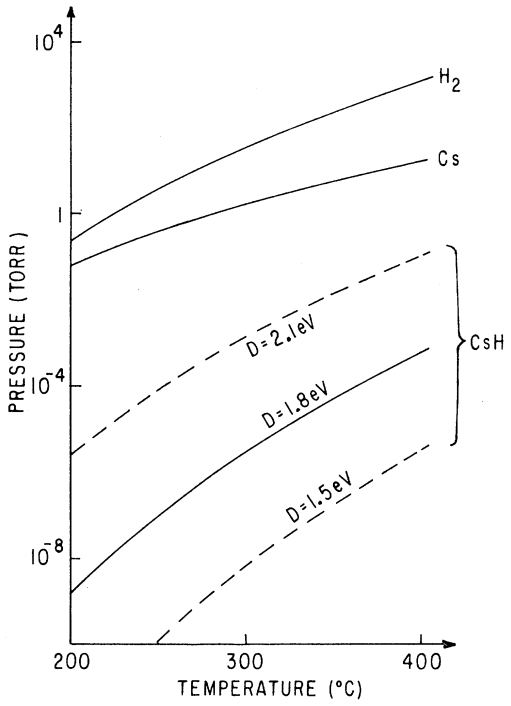

FIG. 3. Partial pressures above the Cs-CsH system.

the rotational structure constants. From Fig. 3 we see that the equilibrium partial pressure of CsH is so low compared to that of Cs that if even a small fraction of the Cs is converted to CsH by the light beam, the vapor will be supersaturated with respect to CsH and condensation of CsH crystals could occur. Although the CsH crystals may be thermodynamically unstable with respect to decomposition into H_2 and cesium (liquid or vapor), the decomposition rates are slow enough to allow the crystals to be observed over a wide range of temperatures.

Two possible mechanisms (besides others) for the light-induced formation of CsH are

$$Cs^*(7P) + H_2 \rightarrow CsH + H + \sim 0.04 \text{ eV} \quad (1)$$

or

$$H_2^{\dagger}(E > 2.7 \text{ eV}) + Cs(6s) \rightarrow CsH + H. \quad (2)$$

It is likely that Reaction (1) is the main mechanism for the particle formation in Cs. If this is also true for other alkali-hydrogen systems, then the phenomenon would open the intriguing possibility of a new and efficient isotope-separation method for alkali metals or possibly other metals too; i.e., if the laser excites isotopic species (atomic or molecular) of the metal selectively, and if the excited species mainly react with H_2 to produce metal-hydride particles, then isotope separation is achieved. If these particles are also strongly charged (as in the CsH case), then collection of these particles could be greatly facilitated. On the other hand, Reaction (2), proposed by Polanyi and Sadowski[13] in another situation, could be the main mechanism, if the vibrationally excited hydrogen $H_2^{\dagger}$ is produced fast enough by quenching collisions.[14] If Reaction (2) is the main mechanism, then it might be important for consideration in the separation of H_2 and D_2, if H_2, HD, and D_2 can be vibrationally excited suitably and selectively.

Particle formation is also observed when Rb mixed with H_2 (150 Torr or more) at 350°C is illuminated with either the 4765-Å or the 4880-Å line of the argon-ion laser. Here, the first step of the process is the production[15] of the $Rb_2(C^1\Pi_u)$ excited molecules. Since substantial isotopic shifts exist for the absorption lines of rubidium atoms or molecules, it appears that rubidium is a good candidate for a first investigation of the feasibility of isotope separation by the present phenomenon.

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New Muonic-Atom Test of Vacuum Polarization*

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In order to check the discrepancy between calculation and experiment in muonic atoms, we have remeasured the $5g$-$4f$ transitions in Pb and the $5g$-$4f$ and the $4f$-$3d$ transitions in Ba. Our new results show no discrepancy and confirm recent theoretical calculations of vacuum polarization to within 0.5%.

The energy levels of muonic atoms can be calculated to high precision by solving the Dirac equation, taking into account corrections for nuclear size and polarization, electron screening, vacuum polarization, Lamb shift, and other smaller effects. Accordingly, precise measurements of transition energies can be used to test the accuracy of these corrections. In particular, certain transitions in medium- and high-Z atoms whose energies are in the 100–500-keV region tend to be relatively insensitive to either nuclear or electron screening effects and so provide a sensitive test of the higher-order quantum-electrodynamics corrections.

The results of an experiment designed to make this test were published by Dixit *et al.*[1] in 1971. Our measurements disagreed with those of Backenstoss *et al.*[2] and with the theory for a number of lines in the 100–500-keV region for several elements. In particular, near 450 keV, the $5g$-$4f$ lines of muonic Pb and the $4f$-$3d$ lines of muonic Ba showed discrepancies amounting to more than 5 times the stated error. Since then, much of the discrepancy has been removed by careful theoretical work (see the review by Watson and Sundaresan[3]). Although the measurements of Walter *et al.*[4] on Hg and Tl confirmed our results, the theoretical calculations had now positioned themselves between the earlier measurements of Backenstoss *et al.*[2] and those of our group[1] and Walter *et al.*[4] In view of this a new series of measurements seemed warranted.

We have in progress such measurements using the muon beam of the Space Radiation Effects Laboratory synchrocyclotron. Although this work is not yet complete, we believe there has been sufficient interest in the subject during the past four years for the results obtained thus far to be reported without delay. A full report will be published in due course.

The techniques used in this experiment were similar to those used before.[1,5] A standard telescope was used to define μ^- stops in each of two targets. The targets were positioned perpendicular to the beam direction and a Ge(Li) detector was placed in the beam directly behind the muon veto counter. The detector had high resolution (525 eV full width at half-maximum at 122 keV and 1050 eV at 468 keV), an area of 1 cm^2, and a small thickness, 0.5 cm, chosen to reduce the