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One-atom detection using resonance ionization spectroscopy*

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A new measuring technique which can detect a single atom of a given kind, even in the presence of 10^{19} or more atoms of another kind, with good space and time resolution, was utilized to study the density fluctuation of less than 100 cesium atoms in a small volume of space filled with inert gases. Repeated measurements of the absolute number of atoms in a defined volume at an arbitrary time were recorded for the first time in order to obtain a statistical distribution giving the fluctuation of the number of atoms around the mean value. Numerous other physics applications of the one-atom detector are briefly described.

I. INTRODUCTION

A method for selective counting of free atoms down to the one-atom level has been an outstanding need in all of modern science. Recently, we pointed out this possibility and then briefly reported[1] on such a method; here we describe it more fully, and we show one interesting application—namely, a direct measurement of the density fluctuation of free atoms.

In order to establish a perspective for one-atom detection, let us assume that one wishes to know how many atoms of a specified type are in a well-defined volume of space at an arbitrary time. Starting with the limit of conventional analytical sensitivity, e.g., 10^8–10^{10} atoms, we know that as the limiting sensitivity increases (for example, 10^4 atoms can be detected) to the point that the number of analytical applications also increases. Below 10^4 atoms a new feature appears; namely, $\sqrt{n}/n$ begins to be detectable and atomic fluctuations can be observed. Thus a whole new class of studies becomes possible. As we continue to increase the sensitivity to the ultimate limit so that just one atom can be detected in the specified volume at any desired time, extraordinary new features develop, e.g., the possibility of detecting very rare species. Suppose the probability that just one atom occupies the volume at time t is $P_1 \ll 1$. With a one-atom detector this probability is directly measurable; it is the ratio of the number of successes to the number of trials. To further clarify this point, imagine a scheme which could be used to detect two atoms but not one atom. In this case we see from Poisson statistics that the number of random events recorder per laser pulse (the probe) would be $\frac{1}{2}P_1^2$, a small quantity compared to the true P_1. Detection of quark atoms, solar-neutrino-induced atoms, or superheavy elements may require one-atom sensitivity.

In our method a laser is pulsed into a defined volume of space at any arbitrary time. All atoms within the volume at that time are ionized and recorded. Thus time-resolved one-atom detection requires pulsed lasers; on the other hand, cw lasers would most appropriately be used to sample a steady-state concentration of atoms. To illustrate this fundamental nature of the new method, we report the first direct study made on the fluctuation of free atoms in a small volume of space. Previously, density fluctuations could only be deduced from such phenomena as Brownian motion or Rayleigh scattering.[2]

II. CONCEPT OF ONE-ATOM DETECTION

The accomplishment of one-atom detection rests on the following basic developments. We have devised[3,4] a photoionization method [resonance ionization spectroscopy (RIS)] for the complete conversion of a quantum-selected excited-state population to ionization, making possible sensitive and absolute measurement of the selected population in a gas. When a pulsed dye laser is tuned to promote an electronically excited atomic state to an intermediate bound state lying more than one-half of the way to the ionization continuum, a second photon from the pulsed laser will complete the resonance ionization process; laser pulses on the order of $1\ \mathrm{J/cm^2}$ of beam area were shown to saturate the process. Alternatively, saturation was accomplished for the $\mathrm{He}(2\,{}^1S)$ singlet metastable state at much less energy per pulse by photon absorption of $\mathrm{He}(3\,{}^1P)$ followed by associative ionization produced when $\mathrm{He}(3\,{}^1P)$ collided with $\mathrm{He}(1\,{}^1S)$.

Recently,[5,6] we have extended these ideas to the resonance ionization of atoms from their ground state by making use of two synchronized pulsed lasers. One of the lasers produces photons of energy $h\nu_1$, which is selected to promote an atom from its ground state to a low-lying excited state. A second laser produces photons of energy $h\nu_2$, which is selected to promote atoms from the low-lying excited state to a higher-lying bound state.

Either of the photons ($h\nu_1$ or $h\nu_2$) can photoionize the higher excited state. Only modest energy per pulse is required for the bound-to-bound resonance transitions, but at least one of the lasers must provide about 1 J/cm^2 to saturate the bound-to-continuum process. Of course, as lasers are developed for the shorter wavelengths, more atoms become amenable to the above three-photon, two-laser ionization scheme, and other atoms become amenable to a two-photon scheme (see below) using only one laser.

Several means are available for the detection of one electron; these include gas proportional counters and electron multipliers that operate in a vacuum. Therefore laser schemes which convert one atom to one ion pair, combined with one of these devices for detecting one electron, offer the potential for one-atom detection. Below we discuss in some detail the use of the proportional counter as an electron detector. Since this version of the method is more general than the vacuum case and is more adaptable to a variety of applications, we choose to concentrate on it.

We pursue now a simplified version of the above plan for one-atom detection by making use of just one laser in a resonance ionization process. Referring to Fig. 1, we note that the Cs transitions $6\,^2S_{1/2} \rightarrow 7\,^2P_{3/2}$ (4555 Å) and $6\,^2S_{1/2} \rightarrow 7\,^2P_{1/2}$ (4593 Å) fall well within the range of flash-lamp-pumped dye lasers. Furthermore, in either case the resonance radiation will photoionize the $7P$ level with reasonable efficiency, since the photoionization process is not too far above threshold. We have here a typical situation with respect to spontaneous radiation from the excited state which must be considered in estimating the required laser-power level for saturated ionization. If we use a pulse laser having a width of 1 to 2 μsec, the $7P \rightarrow 7S$ radiations are not of particular importance because these routes back to the ground state through the $6P$ levels are all faster than 1 μsec, and these are recycled. However, the $7P$-to-$5D$ routes are

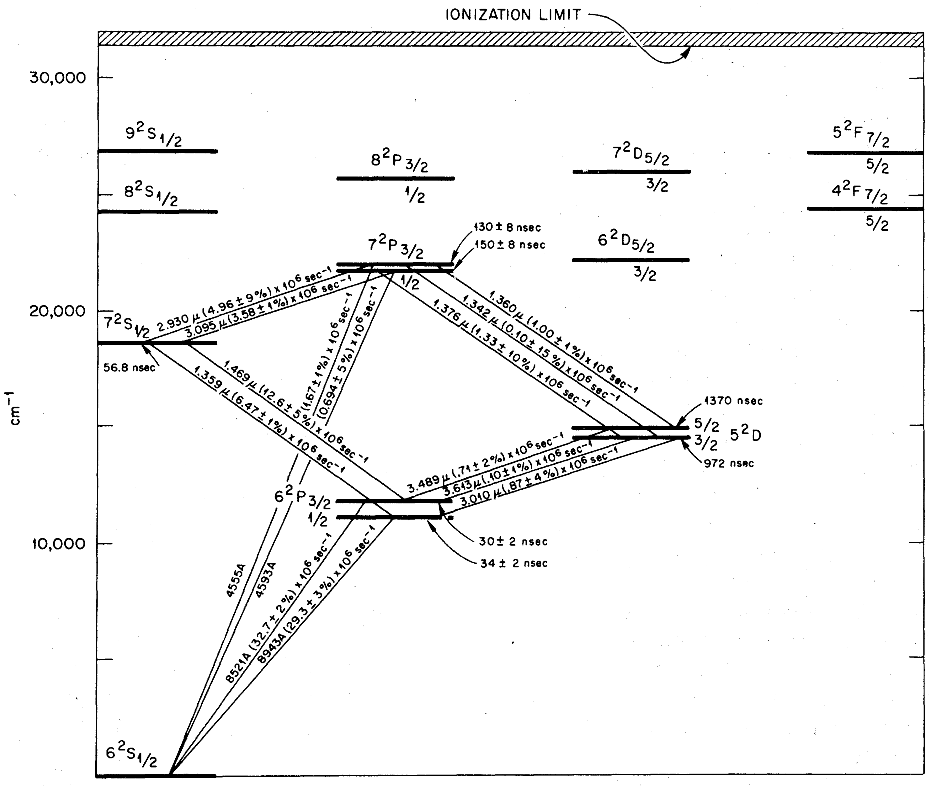

FIG. 1. Spectrum wavelengths, transition rates, and lifetimes for lower levels of the cesium atom. The references for the lifetimes are: $6\,^2P_{1/2}$: a,b; $6\,^2P_{3/2}$: b, c, d; $5\,^2D$ and $7\,^2S$: b; $7\,^2P$: e. References for all transition rates are b (weight = 1) and f (weight = 2); the "errors" are differences between weighted mean and Ref f. (a) A. Gallagher, Phys. Rev. 157, 68 (1967)—Hanle effect. (b) O. S. Heavens, J. Opt. Soc. Am. 51, 1058 (1961)—Bates and Damgaard calculations. (c) E. L. Altman, Opt. Spectrosc. 28, 556 (1970)—lifetime. (d) R. W. Schmeider *et al.*, Phys. Rev. A 2, 1217 (1970)—Hanle effect. (e) P. W. Pace and J. B. Atkinson, Can. J. Phys. 53, 937 (1975)—laser fluorescence. (f) M. Fabry and J. R. Cussenot, Can. J. Phys. 54, 836 (1976) [English Translation: J. Quant. Spectrosc. Radiat. Transfer 16, 127 (1976)] —quantum mechanics; some experimental values for higher levels. Courtesy of Professor Ray Hefferlin, presently at Oak Ridge National Laboratory on sabbatical from Southern Missionary College.

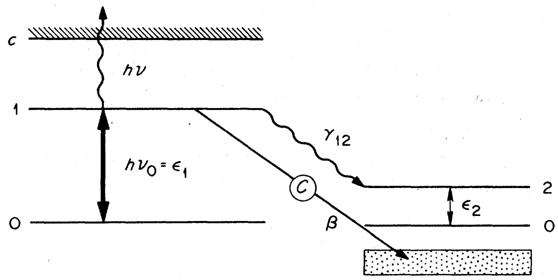

FIG. 2. Schematic of the two-photon resonance ionization process. Radiation to a possible inaccessible state 2, where $\epsilon_2 + h\nu < \epsilon_c$, whereas for state 1, $\epsilon_1 + h\nu < \epsilon_c$ is included. The shaded low-energy zone represents chemical products which are created out of reaction with the intermediate state 1.

of more concern because the $5D$ level has a lifetime of about 1 μsec, and thus atoms can accumulate here during the laser pulse. But these states will also be photoionized by the laser pulse with very good efficiency, since the photoionization process from $5D$ is just above threshold. Whereas radiation processes complicate the measurement of excited-state photoionization cross sections, they are often of less consequence to the saturation of the photoionization.

To pursue the above arguments in a more rigorous way and to obtain results which are of more general value, let us consider very briefly the schematic process shown in Fig. 2. A laser of bandwidth $\Delta\nu$, centered about ν_0, causes the ground state 0 and the intermediate state 1 to quasiequilibrate. In this view the rates of absorption and stimulated emission are much greater than the sum of the rates due to photoionization, radiation to inaccessible states 2, and the rate of conversion through chemical processes. We assume that a pulsed laser provides a constant photon flux equal to $\dot{\phi}$ during its pulse width T, so that the total photon fluence is $\phi = \dot{\phi}T$. Also, we let $\sigma_1(\nu)$ be the photoionization cross section of state 1 at the frequency ν, A the area of the laser beam, L the length of the laser beam defined by the ionization detector, n_0 the total number of atoms in the volume $AL = v$ in the ground state 0 before the laser is pulsed, $n_{0,1}(t)$ be the number of atoms in the states 0 and 1, respectively, as a function of time t where $0 \le t \le T$, $g_{0,1}$ the statistical weights of states 0 and 1, respectively, γ_{12} the rate of spontaneous decay from state 1 to state 2, and β the rate of destruction of state 1 due to all collision processes.

Even at modest laser power, $\dot{\phi}(\nu_0)$ is great enough at the resonance frequency ν_0 to keep states 0 and 1 in equilibrium, thus, at any time,

$$n_1(t) = (g_1/g_0)n_0(t)\,, \tag{1}$$

and at time $t = 0$,

$$n_0(0) + n_1(0) = n_0\,. \tag{2}$$

The rate of change of the population $n_0(t) + n_1(t) \equiv n_{01}(t)$ is given by

$$-\frac{d}{dt}n_{01}(t) = \sigma_1\dot{\phi}n_1(t) + \gamma_{12}n_1(t) + \beta n_1(t) \tag{3}$$

$$= \frac{g_1}{g_0 + g_1}(\sigma_1\dot{\phi} + \gamma_{12} + \beta)n_{01}(t)\,, \tag{4}$$

whose solution is

$$n_{01}(t) = n_0 \exp[-(\sigma_1\dot{\phi} + \gamma_{12} + \beta)g't]\,, \tag{5}$$

where

$$g' = g_1/(g_0 + g_1)\,.$$

We are interested in the number of states in the continuum n_c at the end of the laser pulse, $n_c(T)$:

$$n_c(T) = \int_0^T \sigma_1\dot{\phi}n_1(t)\,dt = \int_0^T \sigma_1\dot{\phi}g'n_{01}(t)\,dt\,, \tag{6}$$

$$n_c(T) = \frac{\sigma_1\dot{\phi}n_0}{(\sigma_1\dot{\phi} + \gamma_{12} + \beta)} \times |1 - \exp[-(\sigma_1\dot{\phi} + \gamma_{12} + \beta)g'T]|\,. \tag{7}$$

Equation (7) shows that to obtain saturation, i.e., each atom which was in the volume v before the laser pulse is converted to an ion pair during the laser pulse, two conditions must be met:

$$\sigma_1\dot{\phi} \gg \gamma_{12} + \beta\,, \tag{8a}$$

$$g'\sigma_1\dot{\phi}T = g'\sigma_1\phi \gg 1\,. \tag{8b}$$

The laser[7] selected for this work has the following specifications. It is a flash-lamp-pumped dye laser which produces a few millijoules over a wide range of wavelengths, has a beam diameter of 3 mm, a linewidth [full width at half maximum (FWHM)] of about 0.7 Å, and a pulse width (FWHM) of 1.2 μsec. With coumarin 2-dye, about 2-mJ pulses are obtained at 4593 Å, or 30 mJ/cm^2 for an unfocused beam, but can be focused to exceed 200 mJ/cm^2.

To examine (8a) we also need an estimate of the photoionization cross section. Zeman[8] obtained 6.2×10^{-18}cm^2 for Cs($7\,^2P_{1/2}$) at $\lambda = 4593$ Å and 8.8×10^{-18}cm^2 for Cs($7\,^2P_{3/2}$) at 4555 Å. Since $\dot{\phi} = 2 \times 10^{23}$cm^{-2}sec^{-1} for 200 mJ/cm^2 in a 2-μsec pulse, $\sigma_1\dot{\phi} = 2 \times 10^6$ sec^{-1}. One expects[9] collisional destruction of excited states to occur at a rate less than $10^4P + 100P^2$, where P is the gas pressure measured in Torr and the rate is sec^{-1}; hence, $\beta < 10^6$sec^{-1} at 100 Torr. Of course, the radiation process at rate γ_{12} can generally be estimated from lifetime and branching-ratio data for a given atom. We observed above in the Cs example (see Fig. 1) that radiation processes are of little consequence because every excited state can be photoionized by the 4555-Å radiation. Condition (8b) is examined as follows: for Cs $7^2P_{3/2}$, $g'=\frac{2}{3}$, $\sigma_1=8\times10^{-18}$ cm^2, $\phi=5\times10^{17}$cm^{-2} (200 mJ/cm^2); thus $g'\sigma_1\phi=2.9$. Equation (7) then shows $n_c(T)=0.95n_0$. However, because of uncertainties in some of the above data and the lack of knowledge on the rate of excited-state chemistry (including the possibility that even traces of impurities could make β large), we must take the point of view that experimental observations of saturation, i.e., $n_c(T)$ behaves asymptotically with ϕ, are necessary conditions for the proof of one-atom detection.

III. POPULATION CONTROL

Because we are interested in a direct study of the fluctuation of a few atoms and, in particular, the detection of a single atom, it is necessary to understand how to control the population of the atoms to be detected as they diffuse through a gas containing a much larger number of inert atoms or molecules. Interesting questions arise as a consequence of the present technique in which a ground-state population of atoms in a laser beam is totally removed during a short laser pulse. For instance, do atoms diffuse into the laser beam (radius r) during the pulse? We take for D_1 (the diffusion coefficient at 1 atm) 0.25 cm^2 sec^{-1}, which is the measured value[10] at low concentrations of Rb in Ar, as representative of an alkali atom in an inert gas, since data for Cs-Ar are not available. The mean spread x of atoms due to diffusion in an infinite space is given by

$$x^2=4D_1(760/P)t\,, \tag{9}$$

where x is in cm, t is in seconds, and P is the pressure in Torr. Let us put $x=r/20$ to get a 10% effect and take $r=0.1$ cm. For a pulse duration of 10^{-6} sec, $P=30$ Torr; thus only below this pressure would atoms diffusing into the beam contribute more than 10% to a signal during a laser pulse. A related question is: At what pressure would diffusion be too low to refill the laser volume between pulses? With t in Eq. (9) equal to the period between pulses, e.g., 10^{-1} sec and $x=2r$, then $P=1900$ Torr. Therefore, to avoid this effect, the gas pressure should be kept below 1 atm.

The slow rate of diffusion of an alkali atom in an inert gas can cause enormous ground-state chemistry effects during the transport of the alkali atom from the source to a laser beam. Consider the transport of atoms evaporated from a small source at a rate of S_0 atoms per second and which leak into an infinite hemisphere filled with an inert gas. At a distance R much greater than the source dimensions, one finds for the concentration of atoms,

$$\rho_0=S_0/4R^2\bar{v}\,, \tag{10}$$

where $\bar{v}$ is the speed of the alkali atom. One can calculate[11] S_0 per unit source area from vapor pressure data; for Cs, we find 5×10^{14} atoms cm^{-2} sec^{-1} at 300 °K. When $R=2$ cm, one finds $\rho_0=4\times10^8$ atoms cm^{-3} above a source 1 cm^2 in area. If Cs reacts chemically, the concentration is reduced to ρ, where

$$\rho=\rho_0\exp(-\sigma_i\rho_i\bar{v}t)\,, \tag{11}$$

and where σ_i is the cross section for Cs to react chemically with an "impurity" at concentration ρ_i, and t is the time for Cs to diffuse from the source to the laser beam. From Eq. (9) we find t to be on the order of 4 sec for a distance of 2 cm and for the inert gas pressure equal to 760 Torr. To ensure that the exponential argument is no more than 1 requires that ρ_i be less than 3×10^{11} cm^{-3} (for $\sigma_i=5\times10^{-17}$ cm^2), which is an impurity level less than one part in 10^8 at 1 atm. In normal circumstances, when one must have large concentrations, the above discussion points out the necessity for ultraclean systems. However, here we take advantage of the process as a means of preparing a very small concentration of atoms for one-atom demonstrations and for fluctuation studies.

IV. LASER PHOTOIONIZATION OF CESIUM-ARGON MIXTURES

Some preliminary experiments were done in a parallel-plate cell in order to establish the feasibility of detecting one atom of Cs in a gas-filled proportional counter. In particular, we investigated experimentally the effects of collisions for the types of gases suitable in proportional counting.

Figure 3 illustrates the cell, which is made of quartz and contains plane electrodes made of nickel. Cesium is contained in a small side arm, and various gases are admitted through the glass valve. The intensity of the laser pulse is monitored by sampling the direct beam with a beam splitter, a stack of neutral density filters, a diffuser, and a photodiode (Fig. 4). The intensity of the laser goes to the x axis of a two-parameter analyzer (Nuclear Data model 160, ND-160). Charge from the ionization of Cs is collected by means of the parallel plates, and the pulses (height S) thus created due to electron motion are amplified for presenting to the y axis of the two-parameter analyzer. With this scheme, the function one seeks, $S(I)$, is displayed on the oscilloscope monitor of the analyzer contents. The scale of S can be converted to the number n_0 of atoms detected as follows. Let S_{in} be the signal at the input of the preamplifier (Ortec preamp, model 113, a voltage-sensitive device); then

$$S_{\text{in}}=\frac{1.6\times10^{-19}n_0}{c}\,\frac{x}{d}\,G(w)\,, \tag{12}$$

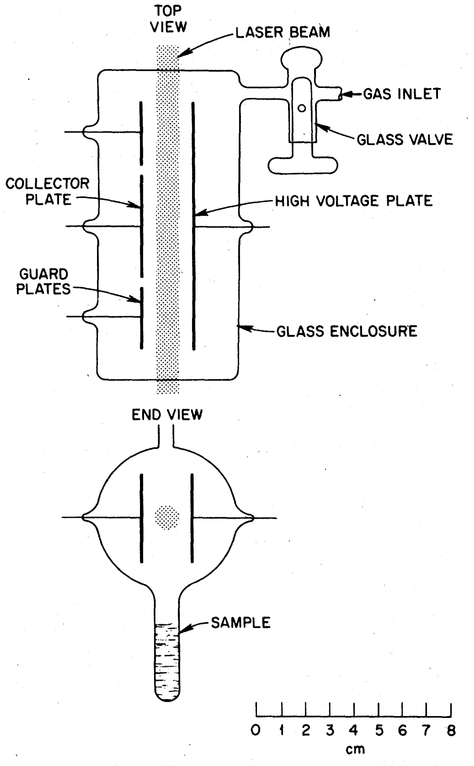

FIG. 3. Schematic design of the parallel-plate cell for resonance-ionization studies. In actual practice, the laser beam was quite narrow (see text).

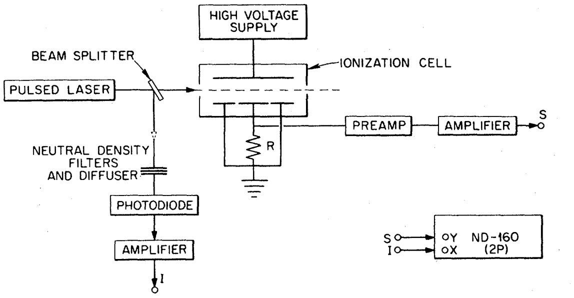

FIG. 4. Experiment arrangement and data-acquisition schematic for the cell experiments. The two-parameter (2*P*) analyzer permits display of the function $S(I)$, directly, where S is the ionization signal and I is the relative laser intensity.

where c is the system input capacitance (here 124×10^{-12} F), x/d is the fraction of the plate separation d (2 cm) traveled by the free electron, and $G(w)$ is a number less than unity which corrects[12] the gain of the amplifier for a pulse of finite rise time which in turn depends on the electron drift velocity w.

We show a sample [Fig. 5(a)] of $S(I)$ for low intensity, i.e., the unfocused beam directed into the cell filled with 800 Torr of argon gas. Note the slight curvature before the long linear region. This behavior is due to the population of the $7\,^2P_{3/2}$ level coming into equilibrium with the $6\,^2S_{1/2}$ level when the intensity becomes greater than a minimum value. At this pressure (800 Torr), there is rapid redistribution among magnetic sublevels; hence, equilibrium populations are governed only by g values. With equilibrium between $6\,^2S_{1/2}$ and $7\,^2P_{3/2}$, $S(I)$ is linear simply because the two-photon process reduces to one-photon ionization of an excited state whose population is not a function of I. For very small I, one expects an I^2 dependence whenever excited-state populations are a linear function of I. In Fig. 5(b) we show $S(I)$ for a case where the laser beam was focused into the cell containing 800 Torr of argon with a lens having $f=50$ cm. The shape of the unfocused beam and the beam divergence were measured with a vidicon detector in a two-parameter, optical multichannel-analyzer system.[13] With the beam focused just beyond the collector plate, we estimated the area to be 2.0×10^{-3} cm^2 at the far edge and approximately 4.4×10^{-3} cm^2 at the near edge of the plate. It appears, therefore, that conditions (8a) and (8b) were met for a low concentration of Cs atoms, even in 1 atm of argon.

During the course of these experiments we observed very sharp resonance on both the Cs($7\,^2P_{3/2}$)

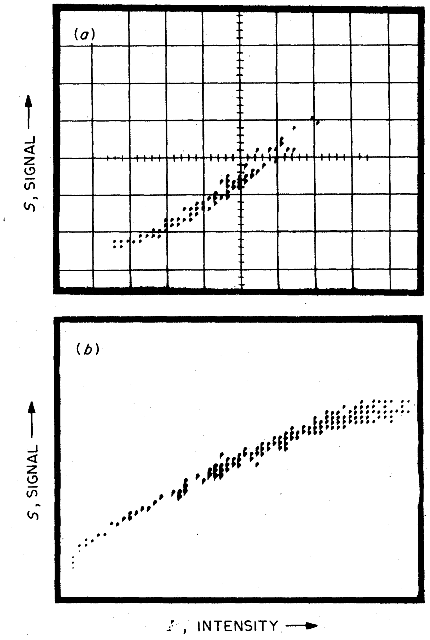

FIG. 5. Sample data obtained with the ionization cell. Part (a) is $S(I)$ for the nonfocused beam of 3-mm diameter and part (b) was obtained with the beam focused as described in the text.

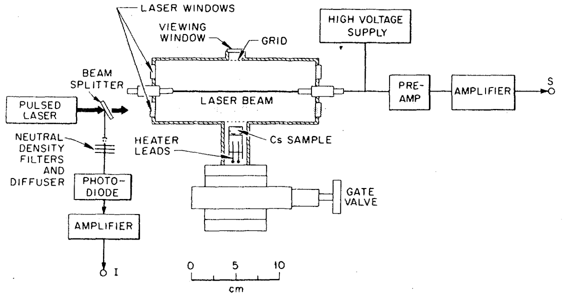

FIG. 6. Schematic of the experiment arrangement and data-acquisition system for the proportional-counter experiments. In case 1, $S(I)$ is plotted as in the cell experiments (see Fig. 4). In case 2, a pulse-height distribution, where the laser pulse produces enough photons to saturate, is plotted.

and $Cs(7\,^2P_{1/2})$ lines; however, with 800 Torr of argon the focused beam showed approximately 10-Å broadening. In the cell experiments, background was seldom a problem except when Cs was condensed on the cell windows. When the beam was directed onto the plates, large photoelectric signals were observed which, of course, persisted over a wide range of wavelengths.

Finally, by changing the position of the laser beam with respect to the Cs source, we observed very large Cs concentration gradients. These gradients were direct proof that ground-state chemistry was occurring at a rapid rate and that our steady-state measurements were taken far from equilibrium, consistent with the discussion in Sec. III. In fact, based on the asymptotic behavior of $S(I)$ in Fig. 5(b), we estimated with Eq. (12) that $n_0 = 1.2 \times 10^7$ in a volume $v = 1.3 \times 10^{-2}\,\mathrm{cm}^3$, or $10^9\,\mathrm{cm}^{-3}$ compared with equilibrium concentration of 6.5×10^{10} atoms cm^{-3} at 300 °K, corresponding to a vapor pressure of 1.8×10^{-6} Torr.

V. DIRECT MEASUREMENTS OF DENSITY FLUCTUATIONS

To demonstrate one-atom detection and to provide a method for observing density fluctuations, a proportional counter was used as the electron detector. A schematic of the experimental arrangement for the proportional-counter studies is shown in Fig. 6. The proportional counter was constructed from gold-plated brass walls equipped with quartz windows, with a wire 2 mils in diameter and a 12-cm active length defined by field tubes at either end. The Cs source could be heated to increase the rate of evaporation of atoms, and it could be positioned at various distances from the laser beam. Thus, according to the discussion in Sec. III, the concentration of atoms in the laser beam could be changed over a wide range. It is important in these studies to avoid electron capture in the counting gas. For this reason, the gas (P-10, i.e., 90% Ar + 10% CH_4) was pumped through the counter—a procedure which avoids the buildup of O_2, a highly electronegative gas.[14]

Calibration of the proportional counter was done at the one-electron level by illuminating the walls with a Hg pen lamp, thus releasing single electrons from the walls at a very low rate. Calibration at the 250-electron[15] level was achieved by placing a weak ^{57}Co source [giving $Fe(K\alpha_1)$ x rays at 6.4 keV] just inside the window. The argon escape peak at 3.44 keV provides another calibration at the 130-electron level.

In the proportional-counter experiments we focused the laser beam below the center of the wire and directly above the Cs source with a lens of 25-cm focal length. With 1-mrad divergence, the beam focused to a 0.025-cm diameter and was approximately 0.10 cm in diameter under both ends of the counter wire, creating a volume of about $5 \times 10^{-2}\,\mathrm{cm}^3$.

The field tubes shown at either end of the counter are held at the appropriate radial potential and are essential to decouple the intense photoelectron signal produced by the laser beam passing through the counter window. Detuning the laser beam from the Cs wavelengths provides a definitive way to measure photoelectric backgrounds. With the field tube arrangement we found that laser background was not detectable. At various concentrations of the Cs atoms we found that the signals showed the narrow resonances characteristic of the Cs transitions at counting gas pressures of 100 to 200 Torr, consistent with the cell observations using pure argon. By gating the analyzers with a sync-out pulse from the laser, backgrounds due to external radiation (such as cosmic rays) were eliminated.

The signals from the wire were coupled to the main amplifier with a charge-sensitive (Ortec 109 PC) preamplifier. The main amplifier had about a 1-μsec rise time and about a 1-μsec decay time. Two kinds of data were acquired as described in the caption of Fig. 6. In the proportional counter, the pulse height produced is proportional to the number of free electrons produced by the primary ionization event (in this case, the laser); it does not depend on where the electrons are produced, provided electrons are not captured.

The data in Fig. 7 shows the function $S(I)$ and its asymptotic behavior at large I. Figure 7 was obtained by using P-10 gas in the counter at a total pressure of 100 Torr. Evidently, CH_4 at this concentration does not drastically increase the rate of chemical destruction of the excited intermediate $Cs(7p)$ states; otherwise, saturation would have been more difficult than it was in the pure-argon case (Fig. 5; see Sec. II). In Fig. 7 the "spread"

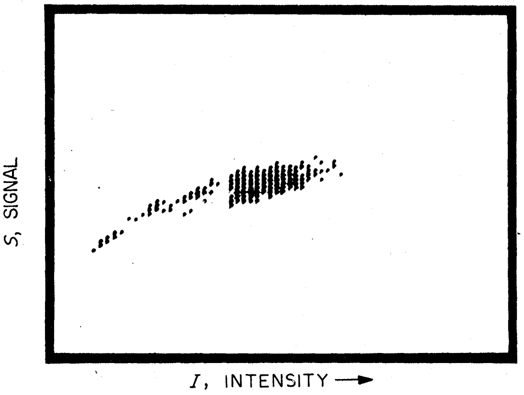

FIG. 7. Two-parameter plot of the pulse heights from the proportional counter vs laser intensity. Data acquired as described in Fig. 6, case 1. Saturated signal corresponded to approximately 1.25×10^4 atoms. At the higher intensity, additional counts were acquired to obtain a pulse height distribution (see Fig. 8).

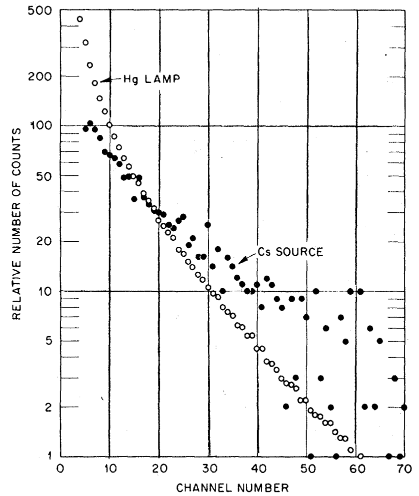

FIG. 9. Pulse-height distribution for case where approximately one count was produced per seven laser pulses. Distribution approaches that of 1 electron produced by an incoherent light source interacting with the counter walls.

in the function $S(I)$ for large I is due to the following: When the contents of the two-parameter analysis memory are displayed on the oscilloscope, the dots near the center of the distribution have a much higher weight than those displaced from the center. The "spread" seen in Fig. 7 does not represent a distribution of pulse height, which is plotted in Fig. 8.

In Fig. 8 we plot a pulse-height distribution for the case where the laser pulses always produced saturation, i.e., the saturated region of Fig. 7. The fluctuation about the mean is comparable to what one expects from the Fe(6.4 keV) x-ray line; however, note the much cleaner distribution in the case of laser ionization of the Cs atoms. The x-ray source produces about 250 electrons[15] per interaction in the peak. From this calibration we see that about 1.25×10^4 Cs atoms were ionized by each laser pulse; an identical number is obtained by using the 130-electron escape peak as a calibration.

It is well known that one electron in a proportional counter produces an exponential-like pulse-height distribution.[16,17] We show such a one-electron calibration in Fig. 9 and compare the distribution to that with the Cs sample in its lowest position and a gas pressure of 100 Torr. In Fig. 10 we

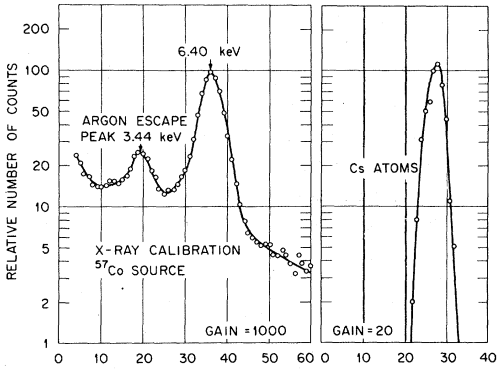

FIG. 8. Pulse-height distribution of signals corresponding to Fig. 7. Only the high-intensity part of the distribution, where the ionization was saturated, could gate the multichannel analyzer (MCA). Comparison of the Cs-atom peak is made with a 6.4-keV x-ray peak (^{57}Co).

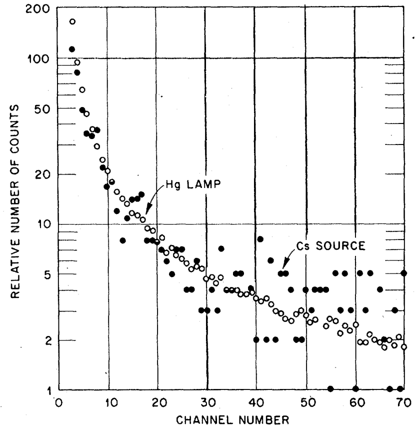

FIG. 10. Pulse-height distribution for case where less than one Cs atom was counter per 20 laser pulses. Distribution is compared with that of one electron produced by an incoherent light source. This distribution is interpreted as that due to one atom in the laser beam. Fluctuations represent counting statistics.

show results at 200 Torr; here we see a Cs distribution that looks very much like the one-electron calibration. Thus, we have detected one atom in the laser beam. By integrating the total number of pulses produced above the normal electronic and laser transient noise, we find that it is not difficult to count directly 95% of the one-atom pulses. At all population levels, including one atom within the laser beam, we observed that the signals vanished when the laser was detuned from the Cs transitions.

A particularly interesting pulse-height distribution is shown in Fig. 11. We recall that the laser samples a small volume of space (0.05 cm^3) and from every atom therein an electron is ejected and counted. Furthermore, we showed in Sec. III that for a range of counting gas pressures the time for diffusion of Cs atoms into the sensitive gas volume is much greater than the time width of the laser pulses and is much less than the time between laser pulses. With these conditions, one may visualize the process of sampling as the successive emptying and refilling of a small volume surrounded by an infinite source of free atoms. By x-ray calibration we find that the distribution in Fig. 11 peaks at 67 atoms and the fluctuation is considerable. We conclude, therefore, that in Fig. 11 we see the fluctuation of atoms in a fixed volume of space. These fluctuations were not previously observable but were deduced from such experimental observations as Brownian motion and the scattering of light.[2]

To analyze the fluctuations in Fig. 11 quantitatively, we turn to the proportional-counter literature involving the Fano factor.[18] The mean number of initial ion pairs produced, $\bar{N}$, is related to the mean pulse height $\bar{P}$ and the mean gas amplification $\bar{A}$ by the following:[18]

$$\left(\frac{\sigma_P}{\bar{P}}\right)^2=\left(\frac{\sigma_N}{\bar{N}}\right)^2+\frac{1}{\bar{N}}\left(\frac{\sigma_A}{\bar{A}}\right)^2, \tag{13}$$

where $\bar{P}=\bar{N}\,\bar{A}$ and σ_N, σ_P, and σ_A are the standard deviations of the indicated quantities. Normally, Eq. (13) is used to evaluate fluctuation of ionization for fixed energy losses in a proportional counter, in which case the σ_N is smaller than that due to random events,[19] a fact that leads to the Fano factor. Here we have a rather different point of view: namely, we assume that σ_N is the standard deviation for the spatial fluctuation of the free atoms of Cs, and for a measured $\sigma_P/\bar{P}$ we can calculate $\sigma_A/\bar{A}$. A Gaussian function was fitted to the data in Fig. 11 for which $\sigma_P/\bar{P}$ is 0.209. Assuming that the free atoms in space obey binomial statistics for random events, $(\sigma_N/\bar{N})^2$ is just $1/\bar{N}$ and $\sigma_A/\bar{A}=1.39$. By comparison, the most elementary theory of the gas amplification process predicts that $\sigma_A/\bar{A}=1$, while deductions[20] from experimental data suggest values somewhat less than 1. From the analysis we conclude that the fluctuation of the number of atoms in a specified volume of space is consistent with a random distribution described by Poisson statistics. Furthermore, we believe that the method described here can help to obtain improved experimental estimates of the Fano factor, because $\sigma_A/\bar{A}$ can be determined quite directly from the laser ionization measurements.

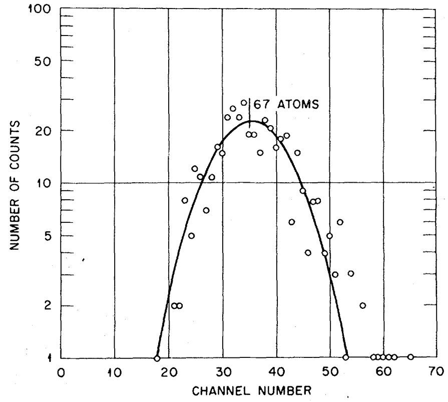

FIG. 11. Pulse-height distribution when most probable number of Cs atoms is 67.

VI. CONCLUSIONS

We have described in detail a system for the detection of one atom. With cesium chosen as an example, we proved that the method is very highly selective so that a single atom of Cs can be detected and identified even in the presence of 10^{19} atoms of another type. There was no indication that this is a limiting separation factor. Moreover, this paper shows the use of the method for a statistical study of the fluctuation of a small number of atoms in a defined volume of space. We discuss below obvious technological extensions of the method and conclude with some examples of applications.

We see no difficulty in making some important extensions of the basic method for one-atom detection. By using two synchronized lasers in the resonance ionization process (see the discussion in the Introduction), it appears possible to detect over one-half of the elements at the one-atom level by using lasers now commercially available. With the higher energy-per-pulse lasers (e.g., 1 J), sample volumes could be greater than 100 cm^3. Work is in progress on the utilization of selectively excited high Rydberg states as intermediates. With states lying close to the continuum, the ionization process can be completed by using electric fields or various kinds of collisions. Photoionization is therefore not required, and the laser energy per pulse needed to saturate a large volume can be drastically reduced (to the mJ range). Furthermore, lifetimes of free atoms (prepared at a known time) can easily be achieved, since our system utilizes pulsed lasers having pulse widths on the order of microseconds.

In further applications, RIS is being used to obtain information on the photoionization cross section for excited atomic states and the rate of reaction of ground-state and excited-state species with various other reaction partners. Studies of the dissociation of atoms from molecules are also in progress for the purpose of atomic identification of classes of compounds.

Many classes of application of one-atom detection have been considered. For analytical chemistry, each advance in sensitivity makes possible new uses. In this paper we took advantage of a sensitivity which permitted for the first time the direct observation of the fluctuation of the number of atoms in a small volume of space. These results indicate that many other interesting areas of atomic fluctuations and statistical physics are open to experimental investigations. Likewise, the measurement of equilibrium vapor pressures below 10^{-17} Torr are now possible, and even straightforward in some cases. In other examples (e.g., the alkali metals) the atomic species at very low concentration may be so reactive that the effects of mass transport rather than equilibrium can be evaluated. Because of the sensitivity now available, very slow transport processes, such as the leakage of atoms through solids and the transport of an atom through great distances in a gas (or the atmosphere), can be quantitated.

Finally, we mention another class of applications: the detection of rare atoms or rare events. In the Introduction we showed that this class of application is feasible only with one-atom sensitivity. Examples of rare atoms are quark atoms,[21] new elements,[22] and nuclear isomers such as fission isomers.[23,24] In other instances, familiar kinds of atoms may be produced but only in rare events; a timely example[25] is ^{205}Pb, which could be produced in small numbers through solar-neutrino interactions with ^{205}Tl.

Note added in proof. We thank Professor V. S. Letokhov for drawing our attention to his talk at the Leon meeting in Norway,[26] in which he independently gave a theoretical discussion of the ultimate sensitivity of the ionization method and possible application to the nuclear isomers.

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