er than the present 11-term result; addition of a further 80 terms improves the SH result by 0.0107, whereas addition of seven terms improves the present result by only 0.0059. Thus the SH 92-term result is better than the comparable present 18-term result by 0.0025. Inclusion of 15 further terms which account for simultaneous correlation in each of the shells gives SH a further improvement of 0.0030 and leads to a result extremely close to the exact value.

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Optical-Pumping Charge-Exchange Method for Studying Nuclear-Spin Orientation in $^1S_0$ Atomic Ions*

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A detailed description is presented of an optical-pumping charge-exchange method for establishing and observing nuclear-spin orientation in atomic ions having a $^1S_0$ electronic configuration. Rb^+, Cs^+, K^+, and free protons have been studied thus far. Various applications of the method include precision measurements of the nuclear moments in the ions and the first measurements of resonant charge-exchange cross sections at thermal energies.

I. INTRODUCTION

In the past, exchange collisions have provided an important mechanism for extending the scope of optical-pumping studies[1] to certain atomic systems that cannot be optically oriented directly. Electron-spin exchange,[2] metastability exchange,[3] and Penning ionization[4] are examples of processes that have been used to transfer spin orientation between optically pumped atoms and other atomic systems of interest. More recently[5,6] we reported on initial successes with another collisional exchange process, resonant charge exchange, which can be used to study singly charged ions and neutral atoms having a $^1S_0$ ground-state electronic configuration. In this paper we will describe in more detail how we have developed this optical-pumping charge-exchange method to make the first studies of nuclear-spin orientation in $^1S_0$ ions. In a subsequent paper we will discuss the application to studying $^1S_0$ atoms.

For measuring nuclear moments, this method with $^1S_0$ ions has the advantage that there is no electronic magnetic moment to complicate the interaction of the system with an external magnetic field. Corresponding measurements of nuclear moments of group IA and IB elements in the parent atoms require separating out the much larger contribution of the electronic magnetic moment. As a result only a few nuclear moments have been measured in such atoms to the few-ppm level.[7,8]

Because the method discussed in this paper is based upon resonant charge exchange, it offers a tool for studying charge-exchange collisions for the first time at thermal energies. Whereas such collisions have been studied extensively at higher energies, there is practically no experimental information in the energy range below 10 eV. In this paper we discuss the determination of cross sections for charge exchange between alkali atoms and ions from linewidths of alkali-

ion magnetic-resonance signals. Other ways of obtaining charge-exchange information with the optical-pumping charge-exchange method have been discussed and carried out recently by others.[9]

II. DESCRIPTION OF METHOD

During a charge-exchange collision, nuclear-spin orientation should be almost completely preserved. As a result of such collisions, atoms with an initial nuclear orientation can become oriented ions, or nuclear-oriented ions can become oriented atoms.

We have applied this concept to establish and observe nuclear-spin orientation in certain alkali ions (Rb^+, Cs^+, K^+) contained with their optically oriented parent atoms in a buffer gas, and to study free protons similarly contained in the presence of exchange-oriented hydrogen atoms. It appears that this method can be used to study most singly charged $^1S_0$ ions having parent atoms with $^2S_{1/2}$ ground-state configurations.

We illustrate the method using our original Rb^+ experiment[5] as an example. In the usual manner for optical pumping (see Fig. 1), circularly polarized Rb D_1 resonance radiation passes parallel to an external magnetic field through a cell containing Rb vapor and a buffer gas, e.g., He or Ne, at about 30-torr pressure. By the process of absorbing and reemitting the resonance radiation, the Rb atoms become polarized, with the coupled nuclear and electron spins each acquiring orientation. A change in the orientation of the Rb atom may be detected as a change in the intensity of light transmitted through the cell.

Rb^+ ions are produced in the cell either by a discharge in a sidearm of the cell or, as was done in some cases, by photoionizing radiation from an external lamp. A nuclear-spin polarization builds up in the Rb^+ ions through Rb-Rb^+ charge-exchange collisions with the oriented Rb atoms. In turn, any change in Rb^+ nuclear-spin orientation has an effect on the Rb-atom polarization through the same Rb-Rb^+ charge-exchange process. In this way, magnetic-resonance transitions in the Rb^+ nuclei may be detected by a change in the Rb-atom-pumping light transmission.

It should be possible to study all alkali-metal ions in the same fashion. For group-IB ions, the parent atoms can be oriented by electron-spin exchange with oriented alkali-metal atoms in the same cell, much as we have done with protons and H atoms (see Sec. V).

The buffer gas serves to minimize spin relaxation of both atoms and ions by slowing down their passage to the cell walls. Since $^1S_0$ ions have only a nuclear moment, their magnetic relaxation in collisions with buffer-gas atoms is very slow and their spin lifetimes can in principle be much longer than for alkali-metal atoms, which have an electron magnetic moment. The only alkali-metal-ion relaxation effect actually observed so far (other than the exchange collisions with the alkali atoms) is diffusion to the walls. Resonance linewidths as narrow as a few Hz have been obtained. There may, however, be other interesting relaxation mechanisms under certain conditions. For example, with the heavier buffer gases, rare-gas atom–alkali-ion molecules might be formed in sufficient numbers that internal molecular interactions (with, for example, the nuclear electric-quadrupole moment) would provide an observable relaxation mechanism.

III. EXPERIMENTAL APPARATUS

Much of our apparatus consists of the standard components of an optical-pumping system. For the lamp we selected a 2.5-cm-diam spherical bulb containing 1.6-torr argon for a starter gas, and excited this lamp by a radio-frequency coil at 10 MHz. We found that the light intensity and stability are enhanced by operating the bulb with a small aluminum heat sink on the tip off to reduce self-reversal problems and to give the alkali-metal pool a larger thermal mass for stability. The length of the heat sink can be "tuned" by removing or adding small pieces at the end to give the optimum light output. By using Corning 1720 glass, we can make a lamp bulb with a lifetime of six months or a year of continuous operation.

We locate the lamp a few feet outside the H_0 field region to minimize light-intensity variations with H_0. Two condensing lenses of 6-in. diam focus the light onto the resonance cell. With the usual D_1 line filters and circular polarizers placed in the light path, the light incident on the resonance cell from the alkali lamps is about 2×10^{15} photons/cm^2 s, as measured with an Eppley thermopile. A typical pump-up time, defined as the time for

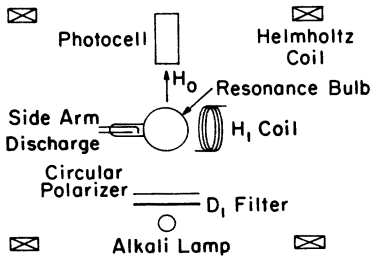

FIG. 1. Schematic diagram of the experimental arrangement for most of the alkali-metal-ion studies.

the pumped atom polarization to reach $1-e^{-1}$ of its final value, is 1 ms. Calculations of the photon flux necessary to produce the measured pump-up times when the lamp output has a 2-GHz width agree with the thermopile measurement of the light intensity.

The resonance cells are mounted together with the H_1 field coils in a thermally insulated box with suitable windows for light transmission. The temperature in the box, which determines the alkali-atom density in the cell, is controlled by a continuous flow of air through it at the proper temperature.

The H_0 magnetic field, generally between 5 and 10 G, is produced by a pair of Helmholtz coils of 30-in. diam mounted with their axis horizontal. A homemade current regulator provides stability of about a part in 10^5 over a few hours, which has proven adequate for the experiments discussed here. For sweeping the field another Helmholtz pair is used. The photodiode used to detect the transmitted light is a United Detector Technology Pin-10. The preamplifier is a low-noise, low-input-impedance, current-to-voltage converter. The combined dark noise of the photodiode and preamplifier is an order of magnitude less than the lamp noise. The output of the preamplifier feeds directly to the input of a Northern scientific 560 model signal averager. The signal-averager sweep output, which is proportional to channel number, sweeps the magnetic field or the H_1 field frequency through resonance.

Most of the resonance cells have been made of Pyrex and most are equipped with discharge electrodes in a sidearm to create the ions. A typical example of a resonance cell is shown in Fig. 2. Tungsten wires enter the discharge region through the glass with ordinary oxide seals. The cathode is a tantalum ring covered with tungsten mesh and spot welded to one of the tungsten wires. The other tungsten wire forms the anode. Electrodeless rf discharges have also been tried with success. In some other cells no discharge is used, and the ions are created by photoionization from an external uv source, a 500-W Hg arc lamp. All cells are cleaned in nitric acid and in HF solution and rinsed in distilled water, and then pumped and baked to 425 °C at a pressure of 10^{-7} torr and held there for a day.

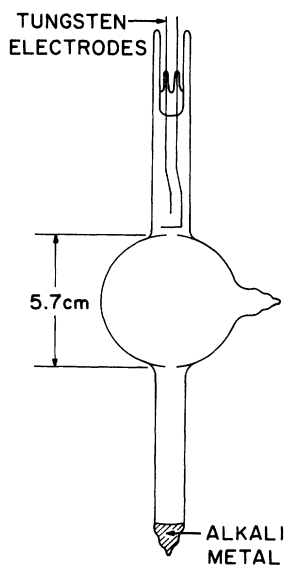

FIG. 2. Alkali-ion resonance cell with discharge electrodes.

FIG. 3. A Rb^+ resonance curve obtained with a low rf field for linewidth studies.

All alkali metals are prepared by reduction and vacuum distilled for purity. After distilling the metals into the resonance cell, the proper amount of buffer gas is admitted through a liquid-nitrogen trap, and the cell is sealed off for use in the experiment.

IV. ALKALI-ION STUDIES

A. Ion Resonance Signals

We have made an extensive study of the Rb^+ and Cs^+ signals. These ion signals can be observed over a wide range of temperatures corresponding to alkali-atom densities in a range from about 10^{-6} to 6×10^{-5} torr. The maximum signal for a 10-ml cell occurs at about 70 °C for Rb^+ and at about 25 °C for Cs^+, where the ion signal is typically a few percent of the atom signal. A Rb^+ resonance curve is displayed in Fig. 3. These signals can be seen under a wide variety of discharge conditions. We have also obtained ion signals using photoionization with a 500-W Hg arc lamp. However, considerable filtering is needed to discriminate against the photoionizing light reflecting into the photodetector. Most of our studies have used the simpler sidearm-discharge method of creating the ions. With photoionization, however, higher buffer-gas pressures can be used, and there are no unwanted discharge byproducts.

As already mentioned, precision measurements of nuclear moments in $^1S_0$ ions offer some advantages, particularly because there is no electronic

moment with its far larger contribution to the Zeeman effect. Although we have not undertaken such precision studies, we have observed both Rb^+ and Cs^+ resonances in magnetic fields as high as 600 G. We obtained linewidths as small as 100 Hz (less than 30 ppm) which we accounted for by the known field inhomogeneity and the charge-transfer rate with the alkali-metal atoms. Other investigators[9] have now measured the magnetic moment in Cs^+ by this method.

B. Linewidth and Exchange Cross Sections

Of some interest are the linewidth and line shape of the ion resonances. At higher temperatures and hence higher alkali-atom densities, the dominant contribution to the linewidth comes from charge exchange with the neutral atoms. In this case, the line shape turns out to be fitted very well by a Lorentzian curve, as expected. At low temperatures there is some residual width which varies with the cell size and buffer gas. Migration to the walls should account for some of this width.

Free electrons are also present in these cells, and through spin exchange with the alkali atoms a free-electron signal also appears[2]. In earlier studies[10] the width of the free-electron resonance line has been shown to be caused mainly by spin exchange with the alkali-metal atoms and to depend linearly upon the alkali-atom density. One might thus expect the widths of the alkali-ion and free-electron resonances in the same cell to change proportionally as the alkali-metal-atom density is varied by changing the cell temperature. Indeed, as is shown in Fig. 4, the Rb^+ and electron widths vary linearly with each other over a wide range of Rb-atom densities. It is also noteworthy that within the experimental uncertainties the slopes are the same for two different buffer gases, He and Ne. A similar linear relationship is obtained between Cs^+ and electron widths in a Cs vapor cell, as shown in Fig. 5.

We can use the slopes of such linewidth comparisons to obtain the ratio of σ_c (the alkali-ion charge-exchange cross section) to σ_s (the electron-spin-exchange cross section) with the same alkali atom. The slope is equal to the ratio of collision rates $\sigma_c v_i/\sigma_s v_s$, where v_i and v_e are the effective collision velocities of the alkali ions and free electrons (generally assumed to be at the same temperature), respectively.

Using the slopes in Figs. 4 and 5 together with the values of σ_s found in the earlier work with electrons,[10,11] we obtain

$$\sigma_c(Rb^+ - Rb) = (7.1 \pm 1.5) \times 10^{-14}\ cm^2,$$

$$\sigma_c(Cs^+ - Cs) = (8.0 \pm 3.0) \times 10^{-14}\ cm^2.$$

These results were obtained for temperatures in the range 20–80 °C, over which σ should vary by only a negligible amount.[12] We believe these are the first measurements of resonant charge exchange at thermal energies. The indicated uncertainties mainly reflect possible errors in

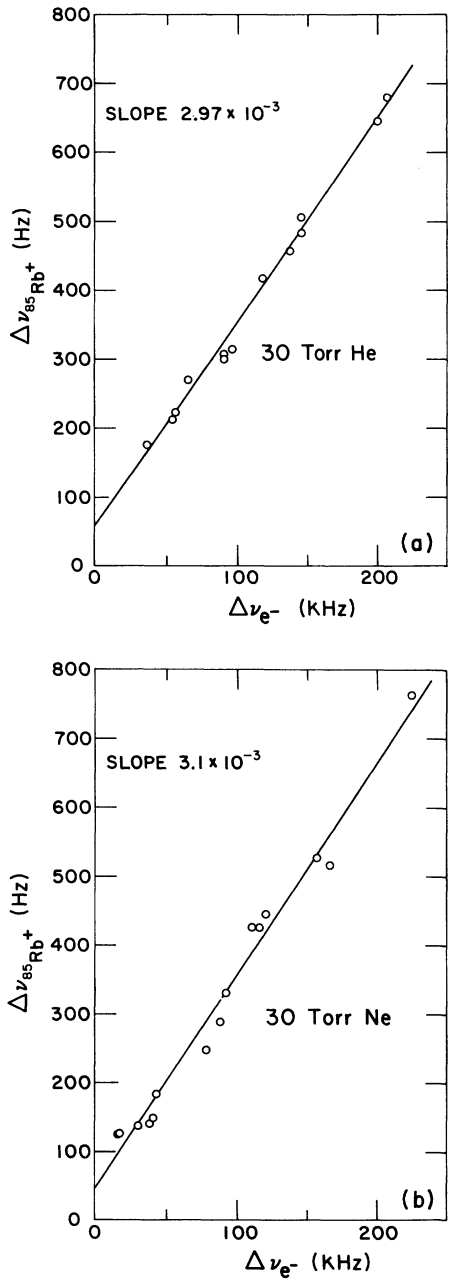

FIG. 4. Graph of Rb^+ resonance linewidth vs electron-resonance linewidth with (a) helium buffer gas and (b) neon buffer gas. Widths extrapolated to zero rf-field broadening.

vapor-pressure determinations of atom density and present uncertainties about the possible contribution of ion molecules to the resonance. Limits on the latter effect may be set by comparing results with different buffer gases. Our value for $\sigma_c(Cs^+ - Cs)$ may be compared with the value of about 1×10^{-13} cm^2 for this cross section, obtained by extrapolation from measurements above 20 eV.[12]

The general behavior of the alkali-ion linewidths, as well as the resonable sizes of σ_c obtained above, are strong evidence that charge exchange is the mechanism determining the spin orientation in the ions. In the forthcoming paper we will present more-complete experimental results, together with an analysis of possible systematic errors in this method of determining σ_c.

C. Ion Densities

We have estimated the ion densities in the cell from the alkali ion and electron signal heights. If we assume that the ions, electrons, and pumped atoms all have the same polarization (which should be true at the higher atom densities), then the ratio of exchange signal to atom signal is given by

$$\frac{S_{ex}}{S_a} = \frac{nJv\sigma_{ex}}{J_a\Gamma_a},$$

where the atoms are exchanging with systems (ion or electrons, as the case may be) which have

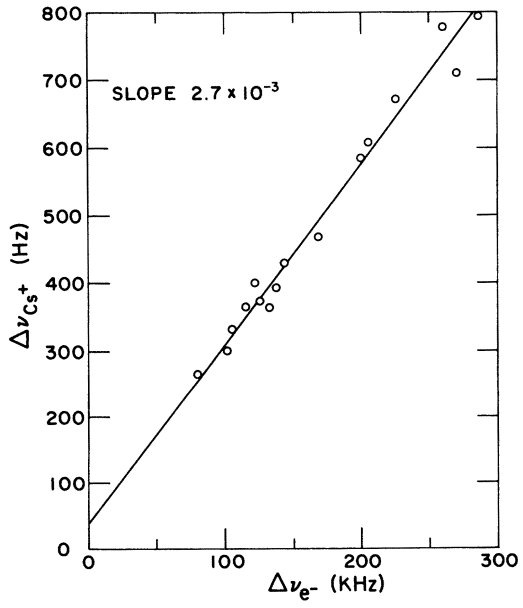

FIG. 5. Graph of Cs^+ resonance linewidth vs electron-resonance linewidth with helium buffer gas. Widths extrapolated to zero rf-field broadening.

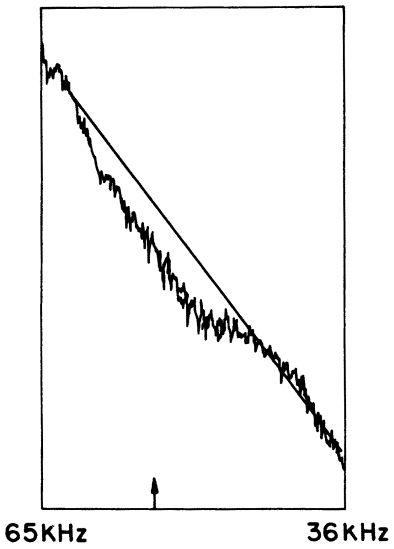

FIG. 6. Proton resonance curve. The arrow marks the expected location of the proton Larmor frequency. The over-all slope is also present without a discharge and results from a change in Rb-atom spin orientation due to the large rf field.

density n, angular momentum J, relative velocity v, and exchange cross section σ_{ex}. The atoms themselves have total angular momentum J_a and total combined polarization exchange rate Γ_a with the pumping light and other systems present.

Our values for σ_c and σ_s, together with the observed relative signal heights of the alkali-metal ions and of the electrons, indicate that about equal numbers of alkali ions and electrons are present, with number densities of about 3×10^{10} ions/cm^3 giving the largest ion signals.

V. PROTON RESONANCE SIGNALS

An atomic ion of fundamental interest is the free proton. Accurate magnetic-moment measurements on the free proton could be compared with recent high-precision measurements of the proton g factor in the H atom.[8] We have employed an extension of the charge-transfer method to produce and detect orientation in protons in a cell containing optically oriented Rb atoms, hydrogen gas, and a helium buffer gas.

The concentration of hydrogen gas in the cell can be raised or lowered with a palladium leak attached to a long tube joining the cell. A sidearm rf discharge produces H atoms and protons (as well as electrons and other ions). The H atoms are oriented by spin exchange with the Rb atoms. Charge transfer between these H atoms and free protons builds up an oriented sample of protons. Spin resonance of the protons is observable

ultimately as a loss of polarization of the pumped Rb atoms through exchange with the H-atom intermediaries.

Using this method, we have observed very broad resonances (Fig. 6) which occur at the proton Larmor frequency and which depend upon hydrogen concentration in the cell, upon H atom polarization, and upon the discharge level. Therefore, we ascribe these resonances to the existence of polarized protons in the cell. We believe that the broad width ($\gtrsim$10 kHz) is a result of free-proton exchange with unoriented protons in H_2 molecules, since there was definite evidence for a decrease in linewidth for lower hydrogen concentration. A typical H_2 partial pressure was about 10^{-3} torr with about 1% dissociated into atoms, as judged by the height of the H-atom signal. In order to obtain narrower resonance lines and larger signals it will be necessary to use a discharge arrangement which produces more complete H_2 dissociation at lower H_2 partial pressure.

VI. SUMMARY AND APPLICATIONS

One of the novel applications of the charge-exchange orientation method is its use in studying the charge-exchange process itself at low energies. Merging-beam techniques seem to offer the only other possibility of studying such processes at energies below the eV range. As discussed in Sec. IV above, the linewidths of the alkali-ion signals can be used to measure charge-exchange cross sections at thermal energies. By similar techniques, one should be able to measure the resonant cross section for most group IA and group IB elements. In addition, cross sections in certain cases of nonresonant charge exchange, such as $Rb^+ - Cs$, should be measurable by the same method. It is hoped that the technical difficulties associated with the proton signal, as discussed in Sec. V, can be met sufficiently well to permit a measurement of $H^+ - H$ exchange, which is of fundamental interest. As pointed out in Sec. III, the formation of molecules composed of an alkali ion and a rare-gas atom might be studied by this method.

Another direct application of this technique is its use in making precision measurements of nuclear moments in $^1S_0$ ions. As mentioned in Sec. IV, we have demonstrated the feasibility of making such measurements to an accuracy of a few ppm. The measurements with the $^1S_0$ ions should be simpler in most cases than nuclear-moment measurements with the parent atoms, which are paramagnetic. A major use of the charge-exchange method should be in measuring nuclear moments to determine hyperfine amomalies for elements in groups IA and IB of the Periodic Table. The method is particularly appropriate for radioactive isotopes because of its simplicity and the small amount of material required.

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