of $H_{ECP}$ to $H_{direct}$ appears to be nearly constant at 0.17 in both systems. These interesting trends as well as those with respect to the whole alkali-atom series will be discussed elsewhere.

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[a] Present address: Department of Physics, Johns Hopkins University, Baltimore, Md. 21218.

[b] Permanent address: Technische Natuurkunde, Technische Hogeschool, Delft, Netherlands.

[c] Present address: Systems and Applied Sciences Corporation, Riverdale, Md. 20737.

[d] Present address: Computer Science Corporation, Silver Spring, Md. 20910.

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# Excitation of the Positronium $1\,{}^3S_1 \to 2\,{}^3S_1$ Two-Photon Transition

Steven Chu and Allen P. Mills, Jr.

*Bell Laboratories, Murray Hill, New Jersey 07974*

The $1\,{}^3S_1$–$2\,{}^3S_1$ transition in positronium has been observed using two-photon Doppler-free excitation. Transitions were induced by a pulsed dye laser, and detected by photoionization of the $2\,{}^3S_1$ state. The resonance signal has a linewidth of 1.5 GHz and a signal-to-noise ratio of 20:1. The frequency agrees with theory to 0.5 GHz. The resonance signal has an amplitude proportional to the square of the laser intensity and displays the expected Stark shift to higher frequency under an applied electric field.

Positronium (Ps), first observed in 1951 by Deutsch,[1] is the purely leptonic atom consisting of an electron and its positron antiparticle. The atom provides a unique opportunity for studying a bound-state two-body system and the quantum electrodynamic (QED) corrections to that system. These corrections to the energy levels of Ps are of particular interest because they contain virtual annihilation terms not found in hydrogen or muonium. Furthermore, unlike these

atoms or hydrogenlike ions, the Dirac equation is not an adequate starting point for deriving the QED corrections in Ps, and the Bethe-Salpeter formalism[2] must be used. Unfortunately, the fully covariant Bethe-Salpeter equation has no known analytic solution and presents formidable calculational difficulties. Nevertheless, Ps is one of the few bound-state systems where the exact Hamiltonian is believed to be known to great accuracy, and precision experiments pro-

vide tests of our ability to understand the two-body problem.

The potential of precision optical spectroscopy on Ps has long been recognized,[3] especially since the pioneering work on the $1S \rightarrow 2S$ transition in hydrogen done by Hänsch and his collaborators.[4] We report here the first observation of the optical excitation of Ps and show that high-precision optical measurements of the Ps energy-level structure are now possible. Our measurements are made possible by (i) the development of high-intensity,[5] pulsed,[6] slow-positron sources, (ii) the discovery of thermal-energy positronium emission from metal surfaces,[7-9] (iii) the development of high-power, narrow-band, tunable laser sources,[10] (iv) the use of two-photon Doppler-free techniques that allow the entire Doppler distribution of atoms to be excited simultaneously,[4,11] and (v) the use of single-atom detection techniques.[12]

The apparatus (see Figs. 1 and 2) consists of a pulsed Ps source, a pulsed laser light source and associated frequency reference, and a single-particle detector. A magnetically transported beam of positrons[9] (1 eV, $4 \times 10^5$ sec$^{-1}$) is produced in an ultrahigh-vacuum system ($2 \times 10^{-10}$ Torr) by a 150 mCi $^{58}$Co $\beta^+$ source and a copper single-crystal moderator cooled[13] to $\sim 100$ K. After passing through a velocity selector, the

positrons are transported into a "bottle" with a magnetic mirror on one end and a grid biased at $+5$ V at the other end. A transverse rf electric field (404 MHz) excites the cyclotron motion of the positrons to prevent them from passing through the magnetic mirror. The positrons are trapped with $\sim 50\%$ efficiency and leak out of the bottle with a $\sim 100$-$\mu$sec time constant. Positrons are extracted from the bottle by applying a 1.25-kV pulse to an accelerator that produces a $\sim 1.5$-m-long harmonic potential well, ($V \sim \text{const} \times z^2$ where $z$ is the $B$ field direction), with a single-crystal copper target at $z = 0$. Since the stored positrons have very little initial longitudinal velocity, they will hit the target after a time corresponding to $\frac{1}{4}$ of the harmonic-oscillator period. Roughly 20 positrons per pulse hit the target in a single bunch with a $\sim 10$-nsec full width at half maximum (FWHM). At the 670 °C temperature of the target, $\sim 5$ of these positrons are reemitted as slow positrons,[14] $\sim 4$ are desorbed from the surface as slow[7,8] $1\,^3S_1$ positronium (mean energy $\overline{E} \cong 0.14$ eV), and the remainder either annihilate in less than 1 nsec at the target or escape as high-velocity positronium ($\overline{E} \cong 3$ eV).

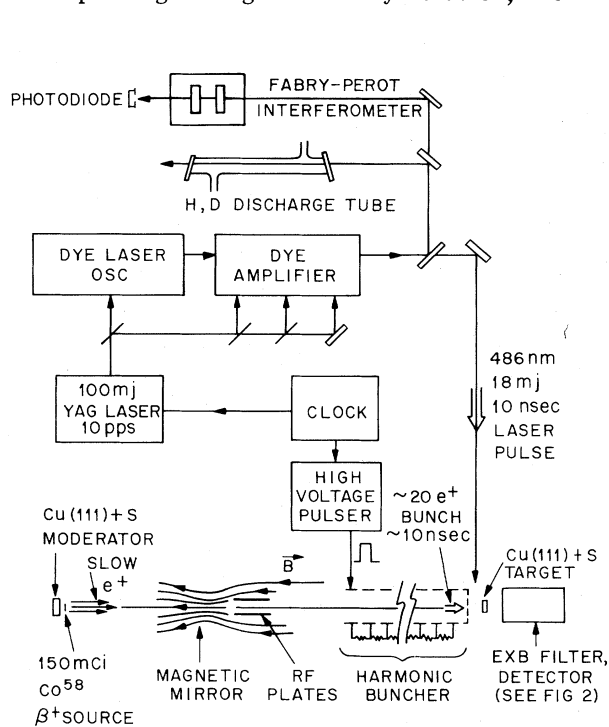The light source used to excite the Ps consists
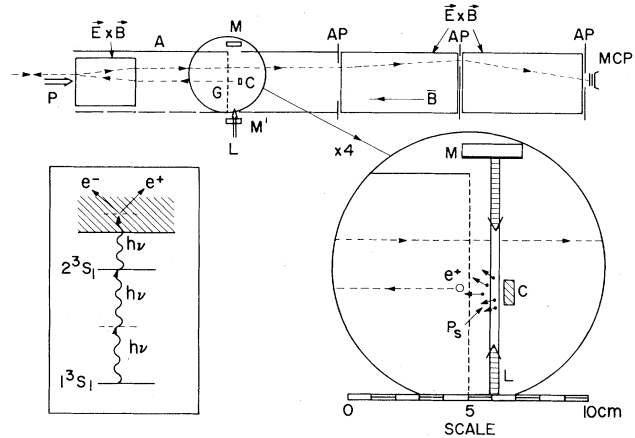


FIG. 1. Block diagram of the apparatus.



FIG. 2. Detail of the positronium-laser beam interaction region. CMA, channel multiplier array detector; AP, aperture; $\vec{E} \times \vec{B}$, $\vec{E} \times \vec{B}$ drift region; $\vec{B}$, 130-G magnetic induction; M, M′, set of three mirrors that causes the laser beam to intersect the Ps in three places and produce counter propagating beams; A, accelerator electrode; C, Cu(111) + S $e^+$ target; G, Au grid; P, $e^+$ pulse incident on Cu target; L, laser pulse; Ps, thermal positronium emitted from the hot target. The dashed line shows path of the $e^+$ ionization fragment. The inset shows the resonant three-photon ionization process.

of a frequency-tripled, $Q$-switched, Nd-doped yttrium aluminum garnet laser (100 mJ/pulse at 355 nm, 12 nsec long FWHM, 10 pps) pumping a pressure-tuned, grazing-incidence–grating[15] dye-laser oscillator with an additional intercavity etalon followed by three amplifier stages. The dye laser produces 18-mJ, ~10-nsec-long pulses to 486 nm in an ~800-MHz bandwidth with <10% amplified spontaneous fluorescence, and is continuously tunable over the $H_\beta$ to $D_\beta$ to Ps $1S$-$2S$ resonances. The frequency of the laser is measured relative to the deuterium ($n = 2 \rightarrow 4$) transitions detected optogalvanically[16] in a Wood's-discharge tube operating with a field of ~30 V/cm, ~10 mA, and ~0.4 Torr of hydrogen and deuterium. A stable Fabry-Perot interferometer frequency marker with a (5.014±0.016)-GHz free spectral range is calibrated on the hydrogen-to-deuterium $n = 2 \rightarrow 4$ isotope shift and allows us to measure the absolute frequency of the laser to within an estimated error of ± 0.5 GHz. Our calibration uses $\nu_\beta(D) = \frac{3}{16}cR_\infty - 161.054$ GHz and $\nu_\beta(H) = \frac{3}{16}cR_\infty - 328.812$ GHz.[17] We have made a 0.8-GHz correction to the frequency scale to account for the measured ac Stark shift of the calibration lines.[18]

We detect the Ps resonance excitation via a three-photon process[19] (see Fig. 2). After the $1\,^3S$ to $2\,^3S_1$ transition is made, the photon flux is sufficient to photoionize the atom in ~1 nsec. Once ionized the $e^+$ fragment is accelerated to ~300 eV and back into the harmonic bunching potential where its motion is reversed. An $\vec{E} \times \vec{B}$ drift region deflects the $e^+$ around the target and into two more $\vec{E} \times \vec{B}$ regions that give velocity discrimination between the positrons and positive ions emitted from the hot target. The positron is then accelerated to ~2.9 kV and hits a two-stage, 22-mm-diam microchannel plate detector with a phosphor screen anode. The electric and magnetic fields are fine tuned on the ~5 prompt slow positrons/pulse that are reemitted from the target. Each detected positron yields a 10-nsec-wide anode signal and a green dot of light that can easily be seen through a window in the back of the vacuum chamber. The overall detection efficiency once the Ps is ionized is ~40%.

We discriminate with 99% efficiency between the copious slow positrons reemitted from the Cu target (~2 counts/pulse) and the ionized Ps by delaying the laser pulse 30 nsec with respect to the $e^+$ bunch. The discriminator output following the channel-plate signal is counted in coincidence with a 30-nsec gate delayed 30 nsec after
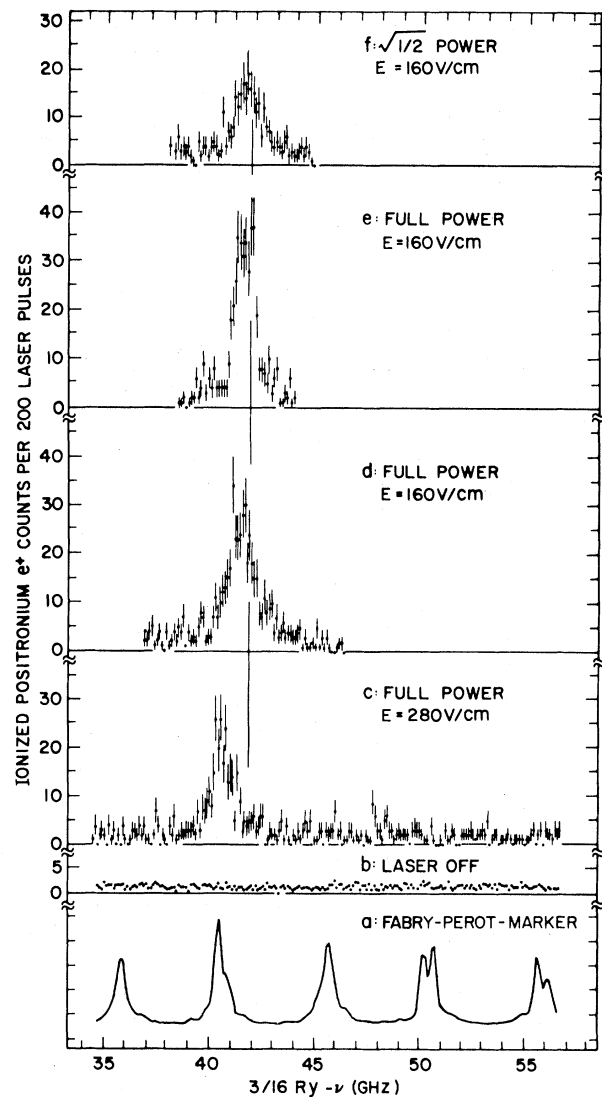


FIG. 3. Ionized positronium counts from the channel plate detector plotted vs laser frequency. (a) Frequency marker signal. (b) Laser-off counting rate. (c) Resonance signal obtained with $E = 280$ V/cm. (d), (e) Same as (c) except $E = 160$ V/cm. (f) Same as (e) but with laser intensity decreased by $\sqrt{2}$. The vertical line shows the line center predicted by Ferrell (Ref. 20) and Fulton and Martin (Ref. 21). The uncertainity in the frequency scale is ±0.5 GHz.

the beginning of the slow-positron signal. The relative time delay between the positron pulse and the laser pulses is measured with a NE 102 plastic scintillator and a 9823K photomultiplier tube (not shown in Fig. 2) that simultaneously detects the annihilation $\gamma$ rays and laser photons entering the light-tight scintillator wrapping through a pin hole.

Figure 3 shows the results of four successive

scans taken within a several-hour period. Figure 3(a) shows the Fabry-Perot frequency marker signal taken simultaneously with the scans shown in Figs. 3(b) and 3(c). In these scans the positron source is pulsed at 100 Hz while the laser is pulsed at 10 Hz, and the additional pulses are used to sample the "laser off" counts shown in Fig. 3(b). The first two scans [3(c) and 3(d)] show the channel-plate counting rate versus laser frequency for two different electric fields in the region between the target and the grid (see Fig. 2). The shift of $0.8 \pm 0.5$ GHz agrees in sign and magnitude with the 0.36-GHz shift expected for the $2\,^3S_1$ state as the electric field is increased from 160 to 280 V/cm. The last two scans [3(e) and 3(f)] show the change in the resonance signal caused by a change in the laser intensity by a factor of $\sqrt{2}$. Since the ionization rate is saturated at our present power levels, the signal shows the expected $I^2$ intensity dependence for a two-photon resonance. No ac Stark shift of the $1S$-$2S$ resonance is detectable at the present precision. The signal observed in Fig. 3(e) corresponds to 0.17 counts per pulse. Given the $\sim 40\%$ detection efficiency, and the estimate that only $\frac{1}{4}$ to $\frac{1}{2}$ of the Ps intersects the laser beam, the $1S \rightarrow 2S$ transition probability is 20%-40%. This agrees reasonably well with our calculated estimate of the two-photon transition rate.

The $\sim 1.5$-GHz linewidths observed in Fig. 3 are attributable to (i) a residual first-order Doppler width due to the divergence and misalignment of the laser beam, (ii) the $\sim 800$-MHz laser linewidth, (iii) the 200-MHz width due to the ionization rate, (iv) a $\sim 100$-MHz second-order Doppler width due to the thermal energy of the Ps, and (v) the nonuniform Stark shift due to inhomogeneous electric fields ($\sim 100$ MHz). The field-free natural linewidth is only the $\sim 1$-MHz contribution from the $3\gamma$ annihilation rates of the $^3S_1$ states.

The line centers in Figs. 3(d)-3(f) are at $\nu = \frac{3}{16}cR_\infty - 41.4(5)$ GHz in agreement with the $\alpha^2 cR_\infty$ calculation of Ferrell[20] (41 000 GHz) and the $\alpha^2 cR_\infty$ corrections of Fulton and Martin[21] (0.812 GHz) which yields a prediction of $\nu = \alpha \times \frac{3}{16}cR_\infty - 41.81$ GHz. The experimental error is dominated by the frequency marker uncertainty. Given an improved laser (cw dye-laser oscillator + pulsed amplifier)[22] and better metrology of the laser frequency one should be able to attain a precision comparable to the hydrogen $1S \rightarrow 2S$ measurements[18] with only a modest improvement in the positronium source. Work is in progress to improve the present observation.

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# Raman Spectroscopy of Argon Dimers

Herman P. Godfried and Isaac F. Silvera

*Natuurkundig Laboratorium der Universiteit van Amsterdam, 1018 XE Amsterdam, The Netherlands*

The first experimental observation of van der Waals molecules by means of Raman scattering is presented. Ground-state rotational and vibrational spectra of dimers of argon were observed in a supersonic expansion. A dipole–induced-dipole model for the dimer polarizability could accurately reproduce the spectra. With use of a seeded expansion the value of the controversial dimer-to-monomer ratio was directly determined as 0.020(4).

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In recent years van der Waals–bound molecules have been the subject of intense research efforts. Their internal properties have been studied by a number of techniques such as laser-induced fluorescence, uv absorption, mass spectroscopy, ir absorption, etc.[1] As a result of the extremely weak signal and small frequency shifts they have never been detected by Raman scattering.[2] This would make possible the direct determination of the rotational-vibrational properties of the ground-state molecule. Indeed, as Weber observed,[3] detection of resolved rotational Raman spectra of van der Waals–bound dimer molecules would constitute a major advance in sensitivity and resolution in Raman spectroscopy. Here, we present the first such spectra of argon dimers. In resolving the rotational spectra for the $v = 0$ vibrational state, we also observed hot rotational bands associated with higher vibrational states. In addition we have observed the vibrational bands. Since these transitions are about 100 times weaker than the rotational transitions, no attempt was made to resolve the rotational structure, as this pushes the limits of our instrumental sensitivity and stability.

A number of experimental reasons have retarded the observation of Raman dimer spectra. First, the intensity is proportional to the dimer density which is at most a few percent of the monomer density. At moderate pressures and temperatures collisional broadening smears out the spectrum which, in addition, is masked by a large background due to collision-induced light scattering. These collisional effects can be suppressed by a reduction in density and temperature.[4] The scattering intensity per dimer is weak since this depends on the square of the anisotropy of the dimer polarizability, which for the rare gases arises mainly from a dipole–induced-dipole mechanism. Finally, the spectra are in the vicinity of the laser frequency and suffer from interference due to Rayleigh and parasitic scattering.

To avoid the collisional problem we produced the dimers in a supersonic expansion which was used earlier to study monomers.[5] This has the additional advantage that substantially lower temperatures can be achieved than the liquefaction temperature of argon, thus simplifying the spectra and their interpretation. From our spectra we could determine both the temperature and the absolute density of the dimers in the expansion.